Removal of cyanide from electroplating wastewater by persulfate oxidation process

Zih-Syuan Wang, Master student of Graduate Institute of Environmental Engineering, National Taiwan University
Yi-Chin Cho, Doctoral student of Graduate Institute of Environmental Engineering, National Taiwan University
Yi-Pin Lin, Professor of Graduate Institute of Environmental Engineering, National Taiwan University

1. Introduction

Cyanide wastewater is generated in many industrial activities (Kim et al., 2018). Cyanide can cause adverse effects on human and aquatic life if discharged into the environments without proper treatments. According to the statistics of Taiwan EPA, electroplating industry is the major source of cyanide wastewater in Taiwan, generating about 4012 tons in 2020. Alkaline chlorination process is the most widely used treatment of cyanide wastewater, but it suffers from several weaknesses, including toxic cyanogen chlorine (CNCl) by-product formation, high amount of sludge generation, and inefficiency for removing metal cyanide complexes. Therefore, advanced oxidation processes (AOPs) has been an alternative for cyanide wastewater treatment (Teixeira et al., 2013; Botz et al., 2016). Several studies have demonstrated the feasibility of using thermal, metal ions, metal oxide, and UV activated persulfate for the removal of cyanide from wastewater (Budaev et al., 2015; Moussavi et al., 2018; Behnami et al., 2021). Most of these treatments require additional equipment or reagents and increase the treatment cost. In electroplating wastewater, many metal ions are present. It was expected that these metal ions could activate persulfate for cyanide removal.

2. Materials and Methods

Batch experiments were performed in a 500 ml reactor at 25 ± 1 ℃. Synthetic cyanide wastewaters were prepared by adding KCN with the pH maintained at around 10.0 in the presence of 0.03 M borate buffer to simulate the basic pH in typical cyanide wastewater and avoid the release of HCN(g) during the experiments. The desired concentrations of peroxydisulfate (PDS) was added into the synthetic solution to initiate reaction under completely mixing. The effects of co-presence of metal ions (1 mM of Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+}), persulfate concentration (1-10 mM), cyanide concentration (2 -12 mM) on cyanide removal and PDS consumption were investigated. The samples were taken at desired time intervals and divided into two tubes for the measurements of PDS and cyanide. Possible by-products including cyanate (OCN^-), nitrate, nitrite, and

ammonia were measured. Additional radical quenching experiments and electron paramagnetic resonance (EPR) studies were conducted to investigate the reaction mechanism. Real electroplating wastewater was used to evaluate the applicability of this process in the industry.

3. Results and Discussions

Influences of water quality parameters on cyanide removal

The influence of metal ions on the activation of PDS and cyanide removal is shown in Figure 1(a). Without any metal ions, 31% of cyanide was removed likely due to the alkaline activation of PDS at pH 10. With the addition of 1 mM of Ni^{2+}, Fe^{2+}, Zn^{2+} and Cu^{2+}, the cyanide removal was 10%, 34%, 53% and 99%, respectively. Cu^{2+} was the most effective in the activation of PDS and was explored in the following experiments. The results obtained using different PDS concentrations showed that 99.3% of cyanide (4 mM) was removed within 20 min and could meet the Taiwan EPA wastewater discharging standard (1 mg/L) when 10 mM PDS and 1 mM Cu^{2+} were used (Figure 1(b)). 89.1%-99.3% of cyanide removal was observed when the cyanide concentration varied from 4-12 mM (Figure 1(c)).

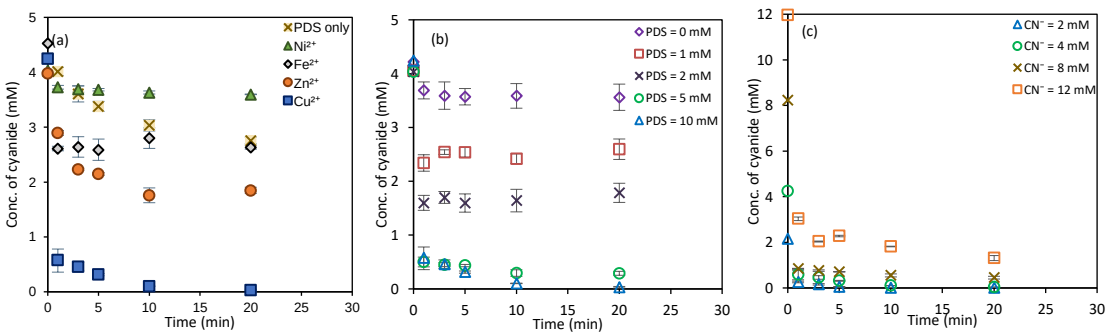

Figure 1. Influences of (a) metal ions (b) PDS concentration and (c) cyanide concentration on cyanide removal. (Experimental condition: initial pH = 10.2, borate buffer = 0.03 M, metal ion concentration = 1 mM, [CN^-] = 4 mM, [PDS] = 10 mM)

Cyanide oxidation mechanism

Radical scavenging experiments were conducted in the presence of methanol, a scavenger for OH · and SO_4^-, to investigate the contribution of free radicals in cyanide removal. Methanol had a slight inhibitory impact on cyanide removal initially within 5 min but had no impact on the final removal (Figure 2(a)). It was speculated that methanol might react with OH · to form organic radicals to remove cyanide.

EPR experiments using DMPO as the spin trap chemical can be used to further confirm the generation of OH · and SO_4^- · and the results are shown in Figure 2(b). In

DI water, no signal was observed. A small signal of DMPO-OH・was found in borate buffer due to the alkaline condition. For borate buffer + PDS, a small signal of DMPO-OH・and a tiny signal of DMPO-SO_4^-・were observed due to the alkaline activation of PDS. A stronger signal of DMPO-SO_4^-・was observed for borate buffer + PDS + Cu^{2+}, which verified that PDS can be activated by Cu^{2+} to form OH・and SO_4^-・for the removal of cyanide.

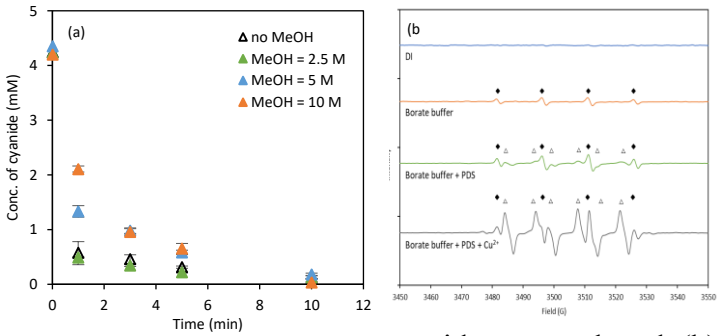

Figure 2. (a) Influence of methanol on cyanide removal and (b) EPR spectra in PDS/Cu^{2+}/CN^- system. (Experimental condition: [CN^-] = 4 mM, [PDS] = 10 mM, [Cu^{2+}] = 1 mM, borate buffer = 0.03 M, [DMPO] = 1 M, ◆: DMPO-OH・, △: DMPO-SO_4^-・)

Application of PDS oxidation process in the treatment of cyanide-containing electroplating wastewater

Real cyanide wastewater was obtained from an electroplating factory. The wastewater contained high concentrations of cyanide (507 mg/L), silver (39.8 mg/L) , copper (241 mg/L), and other metals ions. 40 mM PDS was added to remove cyanide. Cyanide was almost removed in 1 min with a small residual (0.59 mg/L) in the end of the experiment. The nitrogen balance as a function of time is shown in Figure 3. Nitrite was the main byproduct detected and its concentration slightly increased over time. The sum of CN^-, OCN^-, NH_3-N, NO_2^-, and NO_3^- was about 4-6 mM, suggesting that nitrogen gas may be generated during the reaction.

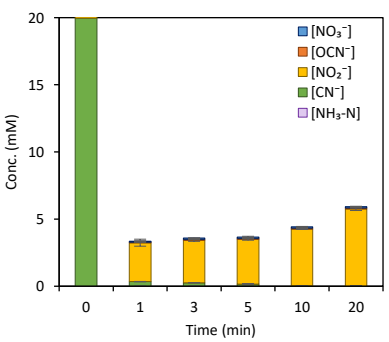

Figure 3. Electroplating wastewater treatment in PDS oxidation process with pH control by using 6 M NaOH. (Experimental condition: total cyanide = 507 mg/L, initial pH = 10.8, final pH = 10.3, [PDS] = 40 mM)

4. Conclusions

Common metal ions present in electroplating wastewater showed the following trends in activating PDS for cyanide removal: Cu^{2+}> Zn^{2+} > Fe^{2+} > Ni^{2+}. The optimal concentration of [PDS] was 10 mM when Cu^{2+} = 1 mM and [CN^-] = 4 mM. Based on radical scavenging experiments and EPR study, Cu^{2+} could activate PDS to generate OH・ and SO_4^-・. Nitrite were the main by-products detected in cyanide removal by the PDS oxidation process. Activation of PDS by Cu^{2+} could be a promising process for efficient cyanide removal in real electroplating wastewater.

5. References

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