

REMOVAL OF CYANIDE FROM DILUTE SOLUTION USING A CELL WITH THREE-PHASE THREE-DIMENSIONAL ELECTRODE

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ABSTRACT

The removal of cyanide from dilute solutions containing free cyanide or cuprocyanide was experimentally investigated using a new electrochemical reactor, three-phase three-dimensional electrode cell. The experimental results were assessed in term of removal efficiency of cyanide. The results showed that the reactor could efficiently remove cyanide from the two solutions. The removal efficiency reached as high as about 93% for the two solutions by electrolysis for 10 min at 20 V cell voltage and 0.16 m³/h airflow. It was also observed that the removal efficiency depended on the applied cell voltage, airflow, interelectrode and initial pH value of the containing-cyanide solution. The former two factors have a positive effect while the latter two have a negative effect on cyanide removal in the experimental range.

Key Words: Three-phase three-dimensional electrode; Electrochemistry; Cyanide; Copper; Wastewater

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INTRODUCTION

Cyanide-containing solution is one of the major effluents for most metal finishing and hydrometallurgical and electroplating industries. Under Code of Federal Regulation 40, Part 261, the U.S. EPA designates a majority of cyanide-bearing compounds as hazardous waste if they are discarded unused (1). In China, regulatory agencies have set point-source cyanide emission limits of the order of 0.5 mg l^{-1} . Thus, it is necessary to treat wastewater-containing cyanide prior to discharge to the environment.

Two common methods for removal of cyanide are chemical oxidation, with hydrochlorine for instance, or electrochemical oxidation. Neither is ideal for attaining the low levels required. Chemical methods may leave an excess of other objectionable chemicals in the water stream and common electrochemical methods are not efficient when the cyanide level drops below 100 mg l^{-1} because of mass-transfer limitations and low current efficiency. This paper addresses the treatment of dilute cyanide solution using a more effective electrochemical method.

Three-dimensional electrode is gaining increased technical importance since it can provide a more extensive interfacial electrode surface which benefit to solve the problem of mass-transfer limitations, comparing with plate-type electrode (2–5). Therefore, it is appropriate to the treatment of low concentration solution (2,5). Several three-dimensional electrodes have been tested to treat cyanide-containing wastewater, such as packed-bed anode (6,7) and reticulated three-dimensional electrode (4). Recently, a new electrochemical reactor, three-phase three-dimensional electrode cell has been developed in our laboratory (8,9). The cell is on the base of combination of packed-bed electrode and gas-diffusion electrode, thus differing from the reported three-dimensional electrode reactor that has only solid and liquid phases (2–5). It may not only provide high electrode surface and promote high mass-transfer rate but also electrochemically generate H_2O_2 to oxidize indirectly pollutants on cathode in addition to anodic oxidation. In this paper, we tempt to approach the feasibility of treating the dilute solution containing cyanide or cuprocyanide using the cell with the three-phase three-dimensional electrode.

EXPERIMENTAL

Materials

A commercial extruded granulated coal-based activated carbon (GAC) was used as the work electrode material in this study. It has an average particle size of 4.3–6.2 mm and an ash content of 8.1%. NaCN solution containing 100 mg l^{-1} of cyanide was prepared using reagent-grade chemicals with deionized water. $\text{Cu}(\text{CN})_n$ ($n = 1-4$) solution containing 100 mg l^{-1} of

total cyanide was prepared by dissolving NaCN and Cu(CN) in deionized water with 1 : 4 C_{Cu}/C_{CN} molar ratios (4) without further purification and pH adjusting except as indicated.

Analysis

The remaining cyanide concentration during electrolysis was determined by a standard method, that is, first distilling HCN and then by spectrophotometer with 3-methy-1-phenyl-5-pyrazolone as color-generating reagent (10a). NH_4^+ and NO_3^- were determined according to the literature 10b and 10c, respectively. IR Spectra were recorded on a Bruker Equinox 55IR spectrophotometer.

Experimental Set-Up

The experimental apparatus is a batch rectangular undivided three-phase three-dimensional electrode reactor as shown in Figure 1. The reactor support was made of plastic with a size of $4 \times 15 \times 14$ cm except as indicated and the anode and cathode (main electrodes) were made of stainless steel plates. The GAC of 430 g as particle work electrodes was packed between the two main electrodes. The compressed air was sparged into the particle electrodes by a micropore plate from the bottom of the reactor. The electric power was supplied with regulated DC power supply.

Experimental Method

Prior to the electrolysis, the cell was pretreated first by soaking with cyanide or cuprocyanide for 24 h in order to decrease adsorption of the

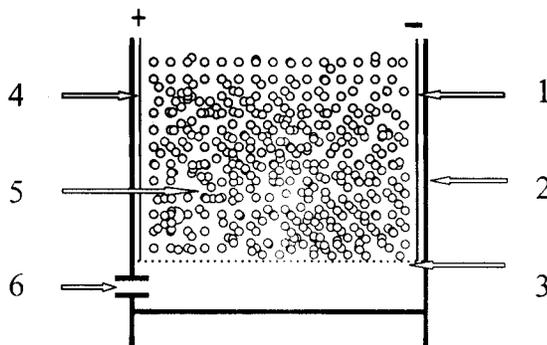


Figure 1. Schematic diagram of the cell with three-phase three-dimensional electrode. (1 cathode; 2 support; 3 micropore plate; 4 anode; 5 GAC particle electrodes; 6 compressed air).

reactants on GAC. Then a total of 270.0-ml of the simulated wastewater containing cyanide or cuprocyanide was fed into the three-dimensional electrode reactor. The reactor was timed starting when the d.c. power and compressed air supply were switched on. The resulting solution was analyzed for remaining cyanide concentration.

RESULTS AND DISCUSSION

Effect of Cell Voltage

The unifying feature for three-dimensional electrodes is that the cell chamber is filled or partly filled with needed working electrode materials depending on the aim of research. In aqueous medium, activated carbon has considerable electrochemical activity (11–13), in addition to its strong adsorption efficiency. Hence it has been receiving increased attention recently for its utilization as an electrode material (14–16). In this present study, the GAC was employed as the working electrode material, also named particle electrodes.

The dependence of cyanide removal efficiency on applied cell voltage at a constant airflow of $0.16 \text{ m}^3 \text{ h}^{-1}$ was illustrated in Figure 2. It can be seen from the figure that the cyanide removal efficiency from free cyanide and cuprocyanide solution increase significantly with increasing the cell voltage from 0.00 to 25.0 V, leading to a maximum enhancement factor of 46.6 and 53.6%, respectively. The increase in cyanide removal efficiency can be simply attributed to the increasing both in current and in the driving force of

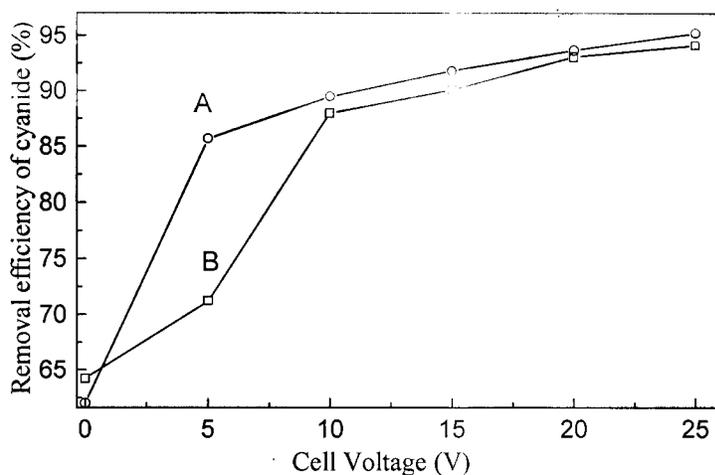


Figure 2. Effect of cell voltage on cyanide removal efficiency. (A: $[\text{Cu}(\text{CN})_n]^{(n-1)-}$; B: NaCN; airflow: $0.16 \text{ m}^3/\text{h}$; batch treating time: 10 min).

electrode reaction as increase in applied cell voltage because potential is the major driving force for the respective phenomena of interest in electrochemical reactor (15). At the same time, it was also observed from Figure 2 that the cyanide removal efficiency from the cuprocyanide solution was always higher than that from free cyanide solution in the range of studied cell-voltage. The observation is consistent with the fact that copper ion has an accelerating effect of cyanide oxidation (7).

Effect of Airflow

During electrolysis, the compressed air was uniformly sparged into the cell by a micropore plate. The sparged air serves two purposes. One is to agitate in order to speed mass transfer. Another is to supply the essential oxygen for electrochemical reactions. Some authors have reported that the oxygen can be changed into a stronger oxidizing agent H_2O_2 on activated carbon electrode by the two-electron reduction of oxygen (17–20). The three-phase three-dimensional electrodes can simultaneously make use of anodic oxidation and cathodic electrogenerated H_2O_2 to degrade pollutants. As a result, it is expected that the sparged compressed air will play an important role in the degradation of oxalic acid.

The cyanide removal efficiencies for different airflow are shown in Figure 3. It indicates that increasing the sparging rate of air from 0.0 to $0.2 \text{ m}^3 \text{ h}^{-1}$ resulted in an increase in cyanide removal efficiency from 77.1 to 95.6% for free cyanide and from 63.8 to 93.0% for complex cyanide. The maximum enhanced cyanide removal efficiencies are 24.0 and 45.8%,

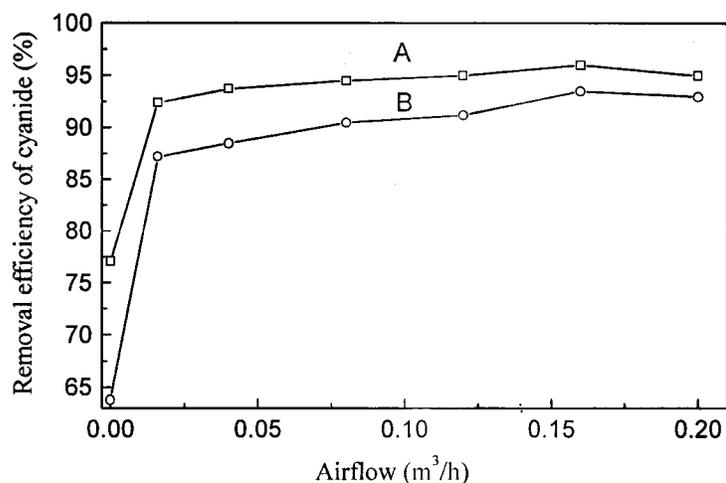


Figure 3. Effect of airflow on cyanide removal efficiency. (A: $[\text{Cu}(\text{CN})_n]^{(n-1)-}$; B: NaCN ; cell voltage: 20.0 V and batch treating time: 30 min for A and 10 min for B).

respectively. It is also found that the two curves rise rapidly below $0.016\text{ m}^3\text{ h}^{-1}$ airflow and then change slowly, almost approach to plateau. The experimental results suggest that the rate-determining step of the cyanide removal was mass transfer when airflow was less than $0.016\text{ m}^3\text{ h}^{-1}$; the cyanide removal rate was mainly controlled by electrochemical reaction above $0.016\text{ m}^3\text{ h}^{-1}$ airflow.

Effect of Interelectrode Distance

To investigate effect of interelectrode distance on removal efficiency of the cyanide, three cells with different interelectrode distances, 15, 30 and 45 cm, were used at the same experimental condition, namely, applied cell voltage (20 V), airflow ($0.16\text{ m}^3\text{ h}^{-1}$), treating time (10 min), packed materials (430 g) and treated solution volume (270 ml). These experimental results are shown in Figure 4. It can be seen from the figure that removal efficiencies of cyanide both fall with increasing the interelectrode distances in approximately linear mode. This situation can be explained as follows. The longer the interelectrode distance, the greater the contact resistance of packed bed, leading to a decreasing in the efficiency of electrochemical reactor. This decreasing denotes the scaling up of the reactor by increasing interelectrode distance will be limited in some extent while the multiple electrode arrangement will be a useful way to scaling up the electrochemical reactor as Ho et al. suggested (7).

Effect of Initial pH Value

The existence forms of cyanide and cuprocyanide are dependent on pH value of solution. It was expected that pH value of solution possibly

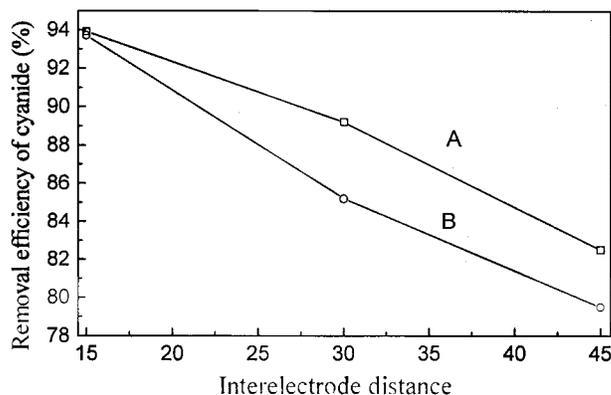


Figure 4. Effect of interelectrode distance on cyanide removal efficiency. (A: NaCN; B: $[\text{Cu}(\text{CN})_n]^{(n-1)-}$; cell voltage: 20.0 V; airflow: $0.16\text{ m}^3/\text{h}$ and batch treating time: 10 min).

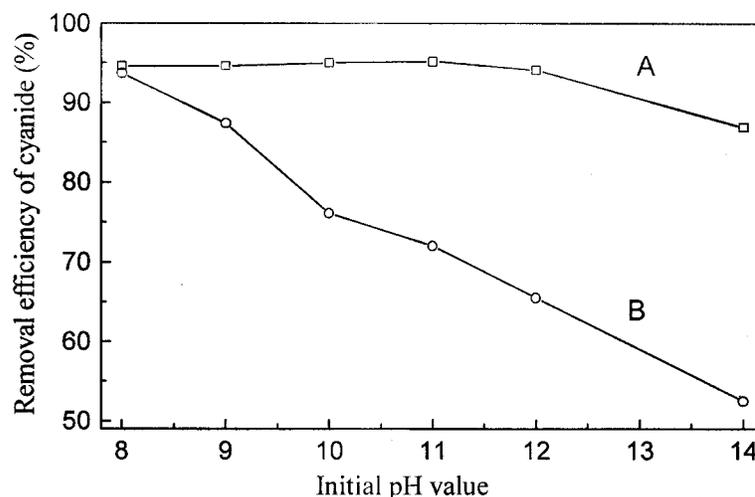
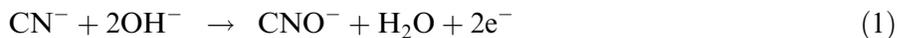


Figure 5. Effect of initial pH value of the wastewater on cyanide removal efficiency. (A: NaCN; B: $[\text{Cu}(\text{CN})_4]^{2-}$; cell voltage: 20.0 V; airflow: $0.16 \text{ m}^3/\text{h}$ and batch treating time: 30 min for A and 10 min for B).

affected electrochemical reactions concerning cyanide removal. Considering that cyanide acid is a rather poisonous volatile compound at acidic condition, the related experiments were carried out in the range of pH 8–14. As shown in Figure 5, the increasing initial pH of free cyanide and the complex cyanide solution both resulted in decreasing in cyanide removal efficiencies. But the decreasing extents are considerably different. The cyanide removal efficiency for free cyanide was reduced only by a factor of 8.1% from pH 8 to 14 while that of cuprocyanide was decreased by 44.0% in the same range of pH. The decreasing discrepancy can be explained as follows. The electrochemical oxidation of cyanide are rather complex, the reaction of primary interest for this study is the two-electron oxidation of cyanide to cyanate which then



proceeds to decompose. From the above reaction, OH^- seems to enhance the oxidation of cyanide, however, there is a strong competing anodic reaction that robs current efficiency.



Furthermore, the reaction (2) can proceed preferentially in an excess of hydroxide (5). For cuprocyanide, in addition to side reaction (2) at basic condition, Cu^+ ion can be electrochemically oxidized to CuO. The product was precipitated at the electrodic surface, foiled electrode and considerably

inhibited cyanide oxidation. The experimental result denotes that, for pollution control, oxidation of cyanide and cuprocyanide proceeds preferentially in the range of about pH 8–9.

Product Analysis

The final oxidation product of cyanide and cuprocyanide is also an interested issue for pollution control because some intermediates of cyanide decomposition may be more poisonous than cyanide itself, in addition to that the detailed mechanism of electrochemical oxidation of cyanide is still controversial. As a result the product analysis of the post-treatment solution for wastewater containing 500 mg l^{-1} cyanide was carried out. In the solution the concentration of $\text{NH}_3\text{-N}$ and $\text{NO}_3^-\text{-N}$ was found to be 5.436 and 0.3997 mg l^{-1} , respectively. They are only a very little part of total nitrogen for 500 mg l^{-1} cyanide (2.02 and 0.15%), suggesting that NH_3 and NO_3^- are not both main products of cyanide oxidation in the three-phase three-dimensional electrode reactor. It is known that the stretching vibration absorption peak of cyanide is in the range of $2260\text{--}2210 \text{ cm}^{-1}$. Figure 6 presents the IR spectrum of the used packed material. No absorption peak was observed in this range. For 500 mg l^{-1} cuprocyanide wastewater, similar experimental results was also obtained. Therefore, it was believed that the final oxidation products of cyanide are mainly carbon dioxide and nitrogen gas. Although it was also believed that the cyanide destruction was carried out possibly by direct anodic oxidation and mainly

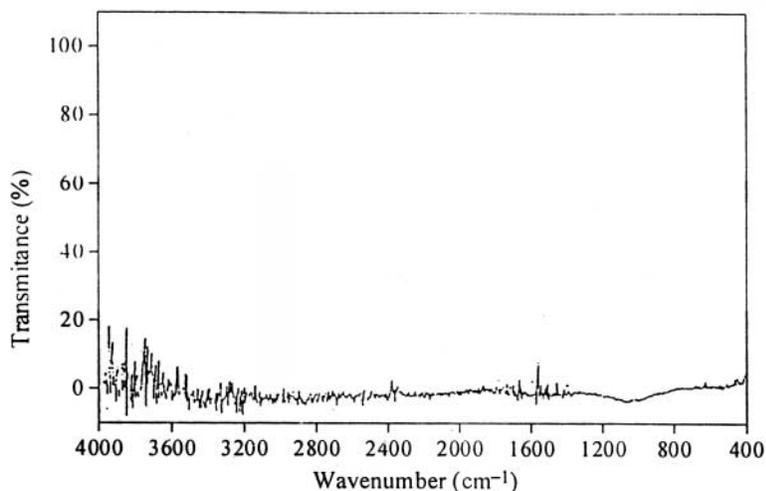


Figure 6. IR spectrum of used packed material.

by indirect oxidation of generated hydrogen peroxide and hydroxyl radical, as shown in Eq. (3), the detail mechanism need further investigations.



CONCLUSIONS

It has been confirmed that cyanide could be effectively removed from dilute solution containing free cyanide or cuprocyanide with a three-phase three-dimensional electrode reactor using GAC as work electrode and compressed air as gas resource. The performance of the electrochemical reactor was considerably affected by applied cell voltage, airflow, interelectrode and initial pH value of the solution. The removal efficiency increased with increase in cell voltage and airflow while increase in the interelectrode distance and the initial pH value resulted in the reduction of the cyanide removal. The removal of cyanide may be contributed to the combination of many factors, such as direct and indirect electrochemical oxidation, and the adsorption of GAC.

ACKNOWLEDGMENTS

This project was supported by National Natural Science Foundation of China (29977030), Natural Science Foundation of Guangdong Province (990274) and Science Technology Project of Guangdong E PA (1999-14).

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