Chemical Engineering Journal 241 (2014) 184–189

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Combined ozone oxidation and biological aerated filter processes for treatment of cyanide containing electroplating wastewater

Jiaqi Cui [a], Xiaojun Wang [a,*], Yanlei Yuan [a], Xunwen Guo [a], Xiaoyang Gu [b], Lei Jian [b]

[a] College of Environment and Energy, South China University of Technology, Guangzhou 510006, China
[b] HuaLu Environmental Technology Co., Ltd., Guangzhou, China

HIGHLIGHTS

- The combined process of BAF–O_3–BAF was suitable for treating cyanide containing EPWW.
- BAF can tolerate higher cyanide toxicity than some other bioreactor.
- High removal efficiencies were obtained with low influent BOD_5/TN in BAF.
- The addition of glucose into raw EPWW could increase the efficiencies of BAF.
- Cyanide compounds of EPWW could be used as the nitrogen source for the microbes.

ARTICLE INFO

Article history:
Received 18 June 2013
Received in revised form 20 August 2013
Accepted 1 September 2013
Available online 8 September 2013

Keywords:
Cyanide
Electroplating wastewater
Ozone
Biological aerated filter (BAF)
Biodegradation treatment

ABSTRACT

In this study, combined ozone oxidation and biological aerated filter (BAF) processes treating cyanide containing electroplating wastewater was investigated. The combined process of first BAF–ozone–second BAF (BAF1–O_3–BAF2) was proved the optimal combined way. Under the optimal condition of 100 mg/L ozone dosage, BAF1 HRT (hydraulic retention time) 9 h and BAF2 HRT 6 h, the CN^-, COD (chemical oxygen demand), Cu^{2+} and Ni^{2+} removal efficiencies were 99.7%, 81.7%, 97.8% and 95.3%, respectively and the effluent CN^-, COD, Cu^{2+} and Ni^{2+} concentrations of 0.16 mg/L, 55.0 mg/L, 0.38 mg/L and 0.41 mg/L, respectively satisfied the discharge standard for electroplating (China). The results show that BAF1 can tolerate higher cyanide toxicity than some other bioreactors. Furthermore, the addition of glucose into raw electroplating wastewater (EPWW) could increase contaminants removal efficiencies of BAF1. Cyanide compounds of EPWW could be used as the nitrogen source for the microorganisms.

1. Introduction

Cyanide is well known for its toxicity and it is an Environmental Protection Agency (EPA) designated priority pollutant, yet is widely used in electroplating industry due to its strong complication and activation ability. Other industries such as gold mining, photo-processing, petrochemical industries, coke-processing plants, metal finishing units and synthetic fiber production also generate large amount of cyanide containing wastewater [1]. To protect the environment and human beings from the hazards of cyanide, effluents containing cyanide must be well treated prior to discharge [2].

The most commonly adopted method for cyanide-contaminated wastewater treatment is the alkaline chlorination oxidation process [1,3]. Although this method can be very efficient in removal of cyanide, it results in highly toxic intermediates (e.g. cyanogens chloride) and suffers from excess hypochlorite which is toxic to aquatic life [4]. Another common method is chemical precipitation by ferrous sulfate due to its low cost and wide availability, but it produces significant amount of hazardous sludge [5]. Other chemical and physical processes, like activated carbon adsorption and ion exchange, also can be employed to degrade cyanide and its related compounds; however, they are often expensive and complex to operate. Biological process has been used in variety of wastewater treatments due to its economic advantages, yet a new technology for cyanide treatment. Several researchers have applied the biological process to remove or degrade cyanide compounds, and reported that cyanide compounds could be utilized as nitrogen and carbon source and degraded by the microorganisms such as fungus, bacteria and algae [6–8]. However, it is well documented that cyanide compounds, especially at high concentration and containing heavy metals, are toxic to the bio-sludge and microorganisms [9]. Therefore, a new treatment method is necessary, which

* Corresponding author. Address: Room 301, College of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, China. Tel.: +86 20 13802767806; fax: +86 20 85640936.
E-mail address: cexjwang@scut.edu.cn (X. Wang).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.09.003

not only can completely remove cyanide but also economically operate and no secondary pollution produced.

Ozone is known as one of the most powerful oxidizing agents with a standard redox potential of 1.24 V in alkaline solutions [10]. Cyanide oxidation with ozone is rapid, and complete decomposition of cyanide can be obtained without undesirable by-products [11]. In this study, ozone oxidation was used as pretreatment process to reduce the toxicity of cyanide and improve wastewater biodegradability. After ozone pretreatment the cyanide and organic matter were further removed by biological aerated filter (BAF), which contains inert media for attached growth of biomass and depth filtration action of suspended solids [12,13]. BAF is an alternative to the traditional activated sludge process which eliminated the requirement of secondary clarification for biological treatment. Furthermore, the attached growth on inert granular media in BAF allows for higher concentration of active biomass than in a suspended growth activated sludge system so that the size of reactor can be reduced [14]. The results of this study derived from a lab-scale test could provide significant information for industrial applications.

2. Materials and methods

2.1. Wastewater source and characteristics

The raw wastewater was cyanide containing electroplating wastewater (EPWW) from an electroplating industrial park located in Zhaoqing city, Guangdong province, PR China. Electroplating wastewater contains heavy metal cyanide complex, all of which are difficult to remove by biological methods. Original and treated wastewater samples were collected daily in clean 100 mL plastic containers. The characteristics of the wastewater and discharge standard for electroplating (China) are summarized in Table 1.

Table 1
The characteristics of raw wastewater.

Parameter	Maximum	Minimum	Discharge standard
COD (mg/L)	329	250	80
BOD_5 (mg/L)	20.1	16.5	–
pH	8.05	7.95	6–9
CN^- (mg/L)	49.0	26.5	0.3
TN (mg/L)	289	266	20
Cu^{2+} (mg/L)	19.5	14.0	0.5
Ni^{2+} (mg/L)	9.80	7.82	0.5

2.2. Experimental installation

Schematic diagram of experimental process was shown in Fig. 1. The main reactors were made of unplasticised polyvinyl chloride. The three reactors were cylinder with diameters of 100 mm. The first biological aerated filter (BAF1) was 1600 mm height, with a working volume of 4.5 L. The second biological aerated filter (BAF2) was 1200 mm height, with a working volume of 3.0 L. The ozone reactor was 1500 mm height, with a working volume of 3.8 L. The reactors were packed with diameter size 3–5 mm ceramic granular media. The media height of three reactors was 900 mm, 600 mm and 700 mm, respectively. Both BAFs were operated in up-flow mode, and the gas–water ratio was 10:1.

The influent was pumped to the bottom of BAF1 by peristaltic pump. The effluent flowed automatically to ozone reactor, then to BAF2. The effluent of BAF2 was collected in effluent tank that could be used to backwash the BAFs once 2 weeks. The accumulated suspended solid (SS) and the excess biomass could be removed in time. And through the change of the pipes and valves, the combined process could be transformed between O_3–BAF1–BAF2 and BAF1–O_3–BAF2.

2.3. Experimental procedure

2.3.1. Single ozone oxidation experiments

In order to study the feasibility of cyanide oxidation by ozone, some tests of single ozonation using cyanide containing EPWW were performed at various cyanide and ozone concentrations. The experiments were carried out in ozone reactor with a maximum ozone production of 3 g/h. The model of the ozone generator was CH-ZTW3G from Guangzhou Chuanghuan Co., Ltd., (China).

Eq. (1) shows the relationship between CN^- removed and O_3 consumption in the ozone reactor. According to Eq. (1), the theoretical mass ratio of O_3 to CN^- is 4.29:1. So the different mass ratios of O_3 to CN^- were chosen for experiments: 1.17, 2.34, 3.51, 4.68, 5.85 and 7.02.

$$2CN^- + 5O_3 + H_2O = 5O_2 + N_2 + 2HCO_3^- \quad (1)$$

Ozone decomposes in the aqueous phase at a rate that depends mainly on the pH of the solution [10]. The ozone decomposition is initiated by hydroxyl ions according to Eq. (2) [15]. So the effect of initial wastewater pH was studied.

$$O_3 + OH^- = HO_2^- + O_2 \quad (2)$$

2.3.2. Combined processes experiments

Two combined ways included O_3–BAF1–BAF2 and BAF1–O_3–BAF2 were investigated to compare the feasibility of them. The activated sludge used for BAF start-up was obtained from a domestic wastewater treatment plant. In the start-up stage, the feed steam was the diluted cyanide electroplating wastewater which was added with glucose (without nitrogen and phosphorus source). The COD concentration was maintained around 400 mg/L. Subsequently the influent CN^- concentration increased each day by adjusting to the proportion of actual wastewater, until removal efficiency of CN^- in BAF was below 50%, which indicated that the start-up had finished. All experiments were performed at 25 ± 5 °C. Experiments with different ozone dosages (80, 100, 120, 125 and 150 mg/L) and hydraulic retention time (HRT, 7.5, 10 and 15 h) were studied.

2.3.3. BAF1 experiments

Sakai et al. [16] concluded that an influent biochemical oxygen demand to total nitrogen ratio (BOD/TN) exceeding 4.9 was necessary for obtaining favorable biodegradation using an oxidation ditch with intermittent aeration. Wang and Liu [17] reported that an increase in TN removal efficiency from 58.1% to 87% by adding sodium acetate into the process to enhance the influent BOD/TN ratio from 2.89 to 8.32. Fujiwara et al. [18] demonstrated a modified influent BOD/TN ratio larger than 4 could result in more organic matter and TN removal efficiency.

In this study, considering the raw wastewater characteristics, BOD/TN ratio was lower than 0.1 that is shown in Table 1. Some efforts were made to improve the BOD/TN ratio for increasing biodegradation rate by adding external carbon source [17]. So different dosages (100, 200, 300, 400 and 600 mg/L) glucose was added in raw wastewater to study the effect of BOD/TN ratio to treatment efficiency of BAF1.

2.4. Analytical methods

During the study, Chinese standard methods for water and wastewater was used for analyzing chemical oxygen demand