

## Recycling of Wastewater Containing Iron-Complex Cyanides Using UV Photodecomposition and UV Ozone Oxidation in Combination with an Ion-Exchange Resin Method

Hirumitsu Wada,\* Kazuko Yanaga, Yasuhiro Kuroda, Sergio Hanela,<sup>1</sup> and Yoshio Hirayama<sup>2</sup>

Nihon Wacon Co., Ltd., 594-32, Higashitoyoda, Hiratsuka, Kanagawa 254-0082

<sup>1</sup>National Institute of Water, Ezeiza, Buenos Aires, Argentina

<sup>2</sup>JICA Industrial Pollution Prevention Project in Argentina JICA Office, Maipu 1300, piso 21, Buenos Aires, Argentina

Received June 23, 2004; E-mail: wada@wacon.co.jp

Wastewater contaminated with iron-complex cyanides was processed by UV photodecomposition accompanied by an iron elimination process using an iron-adsorbent. The wastewater processed by UV photodecomposition was oxidized by ozone combined with UV irradiation. The treated water was deionized by an ion-exchange resin method. This combined processes further increased the production of the pure water volume compared to a single process using an ion-exchange resin. The technique developed in this study can be summarized as follows. First, the iron-complex cyanides in plating wastewater were converted into aquapentacyanoferrate(III)  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$  ion. Following the application of UV irradiation, it was decomposed into iron and cyanide ( $\text{CN}^-$ ) ion. The iron was removed from the water in the form of  $\text{Fe}(\text{OH})_3$  by processing the wastewater with ozone and an iron-adsorbent. The  $\text{CN}^-$  ion was oxidized to the cyanate ( $\text{OCN}^-$ ) form by UV ozone oxidation in a relatively short time. The processed water was de-ionized by passing through cation and anion-exchange resins. The deionized water could be reused as rinsing water in a plating process. The results reported here suggest that wastewater contaminated with chemically stable iron-complex cyanides can be effectively recycled.

In recent years, there has been increasing interest in developing methods for wastewater treatment without using chemicals that do not cause secondary pollution.<sup>1</sup> This process has a high possibility of being practically applied for recycling water from wastewater.<sup>2</sup> The authors surveyed the present status of wastewater in several plating factories in Buenos Aires (Argentina) and Tokyo (Japan). Wastewater from the cyanide plating process generally contained alkaline chemicals (KOH,  $\text{Na}_2\text{CO}_3$ ), metal ions ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , iron ion), cyanide ion ( $\text{CN}^-$ ), iron-complex cyanides, and organic matter, such as tartaric acid  $[\text{CH}(\text{OH})\text{COOH}]_2$  or surfactants.<sup>3</sup> Copper cyanide is used to perform plating to the surface on an iron material. Since copper cyanide plating provides good adherence between the plating layer and the iron surface, it is introduced into the first stage of the plating processes. Therefore, a plating factory usually discharges cyanide wastewater. The iron-complex cyanides are easily formed when iron and  $\text{CN}^-$  ion coexist in waste water. When chemically stable iron-complex cyanides are once formed, it becomes difficult for them to decompose through the conventional chlorination method.<sup>4</sup> The removal of iron-complex cyanides from wastewater produced during the plating process is difficult because iron-complex cyanides have higher chemical stability than other cyanide-containing compounds.<sup>5,6</sup>

The use of UV photodecomposition combined with a low-pressure mercury lamp has been shown to be highly effective for decomposing hexacyanoferrate(II)  $[\text{Fe}(\text{CN})_6]^{4-}$ , which is one of the most common iron-complex cyanide contaminants

in alkaline water.<sup>7,8</sup> Under the influence of UV irradiation,  $[\text{Fe}(\text{CN})_6]^{4-}$  in alkaline water was decomposed to iron and  $\text{CN}^-$  ions via a  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$  intermediate.<sup>9</sup> However, when iron and  $\text{CN}^-$  ion coexist in alkaline water, the original iron-complex cyanides can probably reproduce. In an attempt to develop a practical recycling system for wastewater contaminated with iron-complex cyanides, we investigated the application of UV photo-decomposition in the presence of an iron-adsorbent and with the continuous addition of ozone. This process is followed by the application of UV-ozone oxidation and de-ionization of the treated water using an ion-exchange resin. The efficacy of iron removal from the water containing iron-complex cyanides was investigated by circulating wastewater through an iron-adsorbent column while applying UV photodecomposition combined with the continuous addition of ozone. As a result of UV photodecomposition, iron-complex cyanides in the alkaline wastewater (pH 12.5) were thought to be decomposed to iron and  $\text{CN}^-$  ion via the  $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$  intermediate. The iron was removed by treating the wastewater with an iron-adsorbent, while simultaneously injecting ozone. The  $\text{CN}^-$  ion in the UV photodecomposed water (which was free from iron) was oxidized to cyanate ion ( $\text{OCN}^-$ ) by UV ozone oxidation. The advantage of this treatment process is that, unlike the conventional chlorination methods,<sup>10</sup> it does not produce salts or chloride, and therefore does not require further treatment.<sup>11</sup> The oxidized water was then passed through both cation and anion-exchange resins. During the cation-exchange resin treatment, the sodium ions from the sodium