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

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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) $[Fe(CN)_5(H_2O)]^{3-}$ ion. Following the application of UV irradiation, it was decomposed into iron and cyanide (CN^-) ion. The iron was removed from the water in the form of $Fe(OH)_3$ by processing the wastewater with ozone and an iron-adsorbent. The CN^- ion was oxidized to the cyanate (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.[1] This process has a high possibility of being practically applied for recycling water from wastewater.[2] 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, Na_2CO_3), metal ions (Cu^{2+}, Zn^{2+}, iron ion), cyanide ion (CN^-), iron-complex cyanides, and organic matter, such as tartaric acid $[CH(OH)COOH]_2$ or surfactants.[3] 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 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.[4] 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.[5,6]

The use of UV photodecomposition combined with a low-pressure mercury lamp has been shown to be highly effective for decomposing hexacyanoferrate(II) $[Fe(CN)_6]^{4-}$, which is one of the most common iron-complex cyanide contaminants in alkaline water.[7,8] Under the influence of UV irradiation, $[Fe(CN)_6]^{4-}$ in alkaline water was decomposed to iron and CN^- ions via a $[Fe(CN)_5(H_2O)]^{3-}$ intermediate.[9] However, when iron and 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 though 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 CN^- ion via the $[Fe(CN)_5(H_2O)]^{3-}$ intermediate. The iron was removed by treating the wastewater with an iron-adsorbent, while simultaneously injecting ozone. The CN^- ion in the UV photodecomposed water (which was free from iron) was oxidized to cyanate ion (OCN^-) by UV ozone oxidation. The advantage of this treatment process is that, unlike the conventional chlorination methods,[10] it does not produce salts or chloride, and therefore dose not require further treatment.[11] 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

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Table 1. Composition of Raw and Treated Water

Processing stage	Sample No.	pH	EC/mS m^{-1}	T-CN	T-Fe	Cu^{2+}	OCN$^-$	COD
				mg dm^{-3}				
Raw wastewater	1	8.5	68	23.0	4.9	7.5	0.0	15.0
	2	8.6	56	24.2	5.1	7.8	0.0	14.1
	3	7.9	40	22.5	3.8	7.0	0.0	12.5
UV photodecomposition with iron-adsorbent (60 min)	1	12.2	71	16.5	0.0	4.5	0.0	13.2
	2	12.3	62	16.8	0.0	4.6	0.0	12.5
	3	12.0	42	15.6	0.0	4.4	0.0	10.3
UV ozone oxidation after UV photodecomposition with iron-adsorbent (2.0 h)	1	10.9	68	0.0	0.0	0.0	7.1	2.2
	2	11.2	52	0.0	0.0	0.0	8.5	2.1
	3	11.0	38	0.0	0.0	0.0	6.9	2.3
Effluent of cation resin column	1	3.6	75	0.0	0.0	0.0	1.5	2.2
	2	3.7	54	0.0	0.0	0.0	1.3	2.0
	3	3.5	39	0.0	0.0	0.0	1.2	2.1
Effluent of anion resin column	1	7.7	0.20	0.0	0.0	0.0	0.0	0.8
	2	7.8	0.17	0.0	0.0	0.0	0.0	0.6
	3	7.4	0.10	0.0	0.0	0.0	0.0	0.5

cyanate are replaced by H^+, and the cyanate ions are decomposed into NH_4^+ and CO_2 by hydrolysis under acidic conditions. The ammonium ions are then adsorbed onto the cation-exchange resin.[12] The electrical conductivity of the effluent from the anion-exchange resin column was found to be less than 0.20 mS m^{-1}, and no cyanide or cyanate was detected in the treated water. The deionized water that resulted from this process can potentially be recycled as rinsing water in the plating processes. In this paper, we describe the results of experiments investigating the decomposition of $[Fe(CN)_6]^{4-}$ in wastewater using UV photodecomposition combined with an iron-adsorbent, UV ozone oxidation and an ion-exchange resin method.

Experimental

Reagents. All reagents were of analytical reagent grade (Wako Pure Chemical Industries, Ltd.).

Apparatus. X-ray diffraction spectra of the MnO_2 and $KMnO_4$ were recorded using a Philips Model PW1830 X-ray diffractometer. The atomic absorption data of metal ions were measured on a Nippon Jarrel-Ash (Model AA-880) atomic absorption spectrophotometer. The ozone concentration was measured using an Ebara (Model EG-2001R) ozone monitor. The pH and EC (Electric Conductivity) were measured with digital pH and EC meters.

Analytical Methods. The T-CN (total cyanide, generic term of free CN^- ion and CN^- ion in cyanide compound), T-Fe (total iron, generic term of dissolved iron and suspended iron), COD (Chemical Oxygen Demand), and pH were measured according to JIS K0101 or JIS K0102. The cyanate ion was analyzed as ammonium ion by the JIS K0102 indophenol-blue method after hydrolysis of cyanate ion into ammonium ion by sulfuric acid.[12]

Preparation of an Iron-Adsorbent. Porous zeolite particles were used as an ion carrier of an iron-adsorbent. By the following processing, manganese oxide gave an oxidation ability to the iron-adsorbent. The zeolite particles [$Z\text{-}(Na^+)_2$; diameter, 0.5–2.0 mm; 2.0 dm^3] was soaked in 0.2 mol dm^{-3} of a manganese(II) sulfate pentahydrate ($MnSO_4 \cdot 5H_2O$) solution (5.0 dm^3) for 180 min. The effect of the $MnSO_4$ can be described by the following equation:

$$Z\text{-}(Na^+)_2 + MnSO_4 \rightarrow Z\text{-}Mn^{2+} + Na_2SO_4. \qquad (1)$$

Next, the Mn^{2+} on the surface of the zeolite particles was treated with a 0.3 mol dm^{-3} potassium permanganate ($KMnO_4$) solution (3.0 dm^3) at 368 K for 120 min to produce a manganese oxide coating, as follows:

$$3Mn^{2+} + 2KMnO_4 + 7H_2O \rightarrow 5MnO_2 \cdot H_2O + 4H^+ + 2K^+. \qquad (2)$$

The manganese oxide coating on the zeolite particles was dried in air at ambient temperature, and was then heated at 473 K for 180 min. As a result of X-ray diffractometory, the manganese oxide sample that was processed at 473 K contained MnO_2 and $KMnO_4$.

Samples. For example, the components of the raw wastewater are given Table 1 (samples No. 1 through No. 3).

Experimental Apparatus. Figure 1 shows a schematic diagram of the experimental apparatus. The experimental apparatus was composed of three types of equipment (① UV photodecomposition, ② UV ozone oxidation, and ③ ion exchange). Wastewater samples (5.0 dm^3) containing T-CN, iron complex cyanides $[Fe(CN)_6]^{3-}$, and Cu^{2+} were filtered through a 1 μm filter ③ and supplied to the UV photodecomposition reactor ④ at a constant rate. The reactor (5.0 dm^3) was equipped with a 40 W low-pressure mercury-vapor lamp that emitted UV rays at wavelengths of 254 and 185 nm. A portion of O_2 in air sent to cool the lamp (at a rate of 2.0 dm^3 min^{-1}) was converted into ozone (0.5 mg dm^{-3}) by a treatment with UV rays at a wavelength of 185 nm. The ozonized air was recycled by bubbling the gas through the bottom of the reactor used to oxidize the sample water.

The water treated with UV irradiation was then passed through an iron-adsorbent column ⑧ (100 mm diameter; 300 mm length; 2.0 dm^3 volume) at a rate of 25 dm^3 dm^{-3} adsorbent/h (25 space velocity, SV25 hereafter). In one of the experiments, all or part of the processed water was returned to the raw water tank. In another experiment, all of the water was collected in a storage tank ⑨ (5.0 dm^3). The treated water was sampled from the outflow of the iron-adsorbent column ⑧ at regular time intervals, and was analyzed after being passed through No. 5C filter paper.

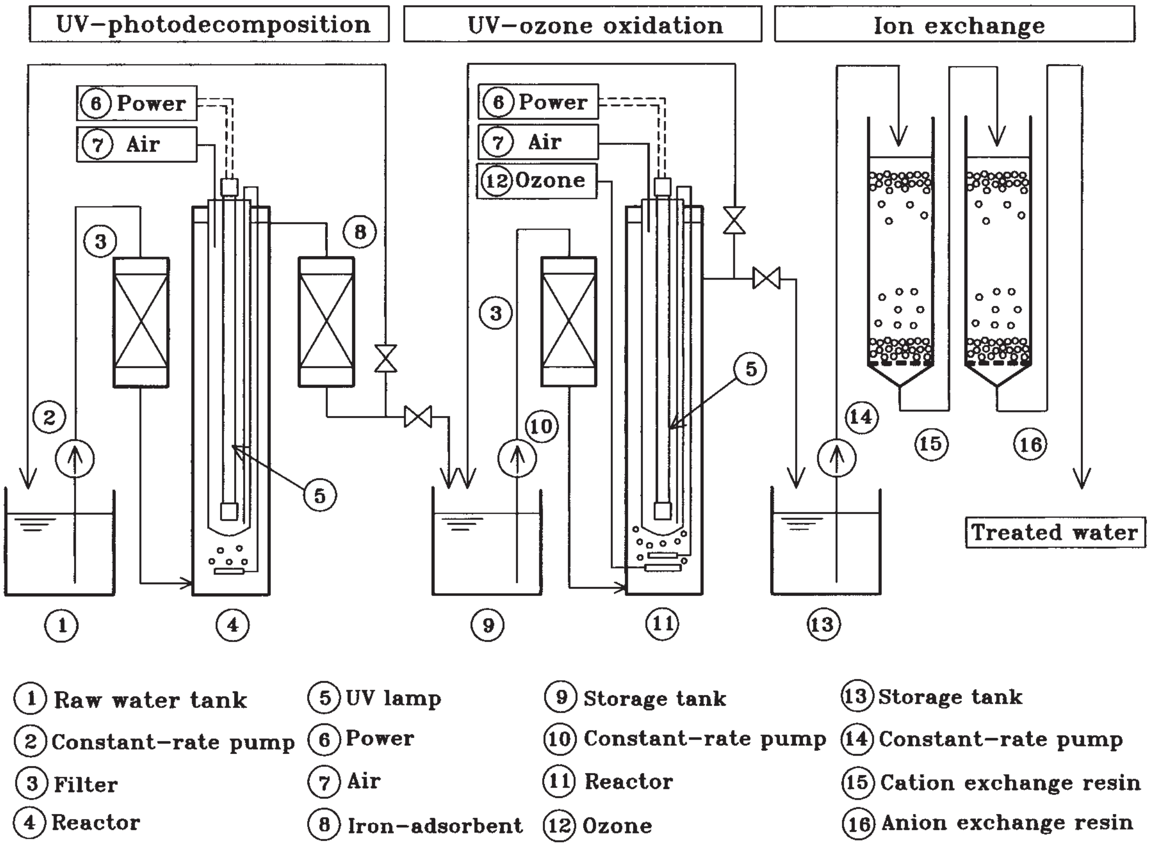

Fig. 1. Schematic diagram of the apparatus to treat iron-complex cyanides wastewater applying combined UV photodecomposition using an iron-adsorbent, UV–ozone oxidation, and ion-exchange method.

The iron-free treated water from the storage tank ⑨ (5.0 dm^3) was filtered through a 1 µm filter ③, and pumped at a constant rate pump ⑩ to a UV ozone oxidation reactor ⑪. The reactor (3.0 dm^3) was equipped with a 40 W UV lamp of the same type as the equipment for UV photodecomposition. Ozonized air was reused by bubbling the cooling air through the bottom of the reactor used to oxidize the water samples. Ozone from another portable ozone generator (generated at a concentration of 5.0 $mg\,dm^{-3}$) was supplied from the bottom of the reactor at a rate of 2.0 $dm^3\,min^{-1}$. The processed water was sampled at regular time intervals and analyzed after filtration through No. 5C filter paper. In one of the experiments, either all or part of the processed water was returned to the raw water tank. In another experiment, all of the water was passed into the storage tank ⑬ (1.0 dm^3). The treated water was sampled at regular time intervals and analyzed for the concentrations of T-Fe, Cu^{2+}, CN^-, OCN^-, and COD after being filtered through No. 5C filter paper. The processed water from the storage tank ⑬ was then passed through two ion-exchange resin columns (diameter, 20 mm; length, 500 mm; volume of resin, 0.12 dm^3) at a constant rate of 2.4 $dm^3\,h^{-1}$. The first ion-exchange column ⑮ was filled with a porous strong-acid type (H-type) cation resin. The second ion-exchange column ⑯ was filled with a porous strong-alkaline type (OH-type) anion resin. The treated water was sampled from the drains of each resin column at the desired time interval. The amount of absorbed material per unit volume of resin was calculated from the treated water volume (the volume of water that passed through the total resin volume), when the electrical conductivity of the effluent rapidly increased.

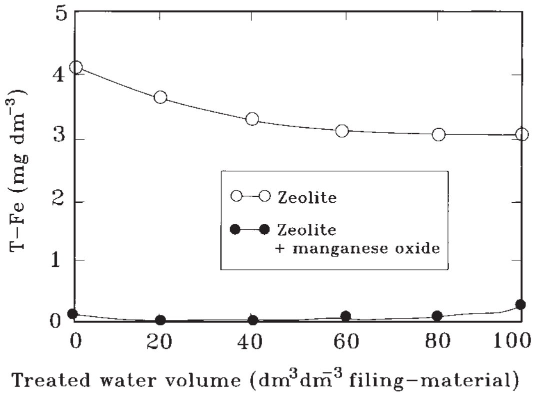

Fig. 2. Relationship between T-Fe concentration of the effluent from the filter column and treated water volume ($dm^3\,dm^{-3}$ filing-material).

Result and Discussion

Table 1 shows the composition of raw wastewater (sample Nos. 1 through 3.

Figure 2 shows the relationship between the T-Fe concentration of the effluent from the filter column and the treated water volume of the pre-treated water by ozone oxidation. The iron(II) sulfate (14.5×10^{-4} mol of $FeSO_4 \cdot 7H_2O$) was dissolved in 40 dm^3 of water. The compounded sample water was pre-treated by ozone oxidation at pH of 12.5. A small amount of ozone concentration of 0.5 mg dm^{-3}, generated by the UV lamp, was bubbled through the bottom of the vessel (50 dm^3) at a rate 2.0 dm^3 min^{-1} for 120 min. This experiment was carried out batch-wise. The pre-treated water was soon passed through the filter column (20 mm diameter; 400 mm length; 0.12 dm^3 volume) at a rate of SV25. The filter column was filled by iron-adsorbent (zeolite material coated by manganese oxide) or merely a zeolite material. The concentration of T-Fe was less than 0.2 mg dm^{-3} during the experiment when applying the iron-adsorbent. For a reference, the pre-treated water was filtered in the same way as mentioned above using the zeolite particles. As a result of the experiment, the concentration of T-Fe decreased to a minimum of 3.1 mg dm^{-3}. However, the iron concentration did not fall any further. Therefore, this method seems to be inadequate to remove iron. The experimental result, which is described above, suggests that the manganese oxide gave the oxidation and elimination ability of iron to the iron-adsorbent.

Figure 3 shows the experimental result of UV photo-decomposition combined with using the iron-adsorbent. The experiment was performed using the part of the UV photodecomposition equipment shown in Fig. 1. The wastewater sample (No. 1 in Table 1) was adjusted to a pH of 12.5 by the addition of 1.0 mol dm^{-3} NaOH. The wastewater was circulated at a rate of 50 dm^3 h^{-1}, and was continuously filtered through the 1 µm filter and the iron-adsorbent column. A rarefied ozone concentration of 0.5 mg dm^{-3}, generated by the UV lamp, was injected through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1}. The ozone was injected into the system at a rate of 60 mg h^{-1}. After 20 min of treatment, the concentration of T-Fe decreased to an undetectable level. The concentrations of T-CN, copper(II) and COD slightly decreased after 60 min. The results of this experiment suggest that the removal of T-Fe takes place in the first 20 min of treatment. This suggests that iron-complex cyanide ($[Fe(CN)_6]^{4-}$) in wastewater[7] decompose at pH of 12.5, and that the removal of T-Fe is complete. This is thought to occur due to the following processes in the reactor:[8,9]

$$[Fe(CN)_6]^{4-} + H_2O + h\nu \rightarrow [Fe(CN)_5H_2O]^{3-} + CN^- \quad (3)$$

$$[Fe(CN)_5H_2O]^{3-} + h\nu \rightarrow Fe^{2+} + 5CN^- + H_2O \quad (4)$$

$$Fe^{2+} + O_3 + H_2O + OH^- \rightarrow Fe(OH)_3 + O_2. \quad (5)$$

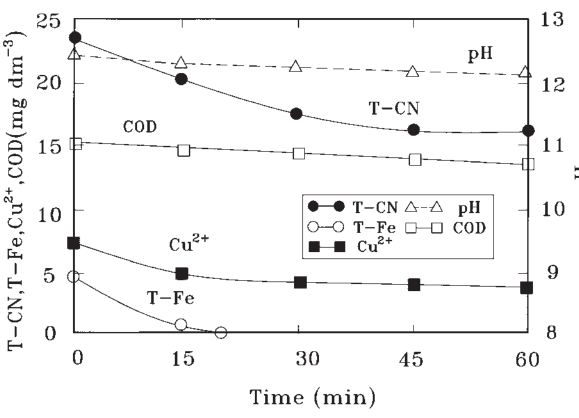

Fig. 3. Variations of T-CN, T-Fe, Cu^{2+}, COD, and pH in UV photodecomposition using the iron-adsorbent.

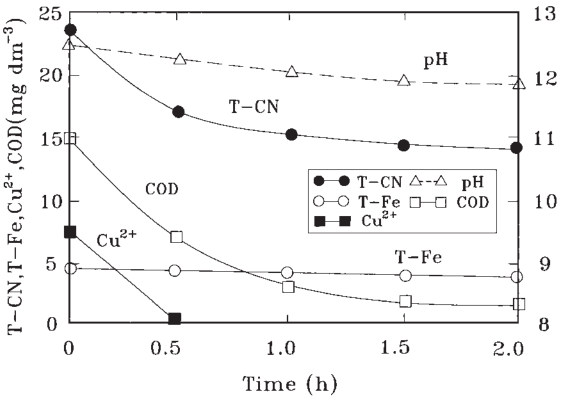

Fig. 4. Variations of T-CN, T-Fe, Cu^{2+}, COD, and pH in UV ozone oxidation without using the iron-adsorbent.

Iron (Fe^{2+}) is also oxidized by $KMnO_4$ on the iron-adsorbent, and seems to change to $Fe(OH)_3$ simultaneously:

$$3Fe^{2+} + KMnO_4 + 7H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + K^+ + 5H^+. \quad (6)$$

It is likely that the $Fe(OH)_3$ is then removed from the sample solution by filtration. However, the removal of T-CN, copper(II), and COD clearly requires much longer treatment times. In the case of this experiment, residual T-CN seems to be free CN^-.

Figure 4 shows the experimental results of UV ozone oxidation without using an iron-adsorbent. The equipment used for the part of UV ozone oxidation is illustrated in Fig. 1. The wastewater (No. 1 in Table 1) was adjusted to a pH of 12.5 using a 1.0 mol dm^{-3} NaOH solution. The wastewater was circulated by continuous filtration at a rate of 40 dm^3 h^{-1}. The processed water was circulated from the raw water tank ⑨ through the filter ③ and the reactor ⑪ and back to the raw water tank ⑨. Ozone from the ozone generator (generated at a concentration of 4.0 mg dm^{-3}) was distributed through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1} to oxidize the wastewater. A rarefied ozone (concentration of 0.5 mg dm^{-3}) that was generated by the UV lamp was also injected through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1}. Therefore, the total amount of ozone injected into the system was 540 mg h^{-1}. After one hour, the COD was less than 5.0 mg dm^{-3} due to the oxidation effects of the COD components, such as tartaric acid, or surfactants as additive chemicals.[3] The reaction time was twice as fast as the oxidation of ozone alone. This is supposedly due to the hydroxyl radicals $(OH)^\bullet$ generated by the 254 nm UV rays and ozone in the water.

$$O_3 + h\nu \rightarrow [O] + O_2 \quad (7)$$

$$[O] + H_2O \rightarrow 2(OH)^\bullet. \quad (8)$$

The hydroxyl radicals $(OH)^\bullet$ appeared to further accelerate the oxidation speed of organic matter. In addition, another radical species $(OOH)^\bullet$ is thought to have been generated by O_2 and electrons (e^-) in the water[13,14] according to the following reactions:

$$O_2 + e^- \rightarrow O_2{}^- \quad (9)$$

$$O_2{}^- + H_2O \rightarrow OH^- + (OOH)^\bullet. \quad (10)$$

Those radical species [$(OH)^\bullet$ and $(OOH)^\bullet$] are thought to exist in the aqueous phase and to quickly attack the organic matter.[15]

For example, tartaric acid is thought to be decomposed to CO_2 and H_2O by the following process:[16]

$$[CH(OH)COOH]_2 + 2(OH)^\bullet \rightarrow [CH(OH)_2COOH]_2 \quad (11)$$

$$[CH(OH)_2COOH]_2 + h\nu \rightarrow 2HOCCOOH + H_2O \quad (12)$$

$$HOCCOOH + 2(OH)^\bullet \rightarrow HCOOH + CO_2 + H_2O \quad (13)$$

$$COOH + 2(OH)^\bullet \rightarrow CO_2 + H_2O. \quad (14)$$

After two hours, the COD level was reduced to 2.0 mg dm^{-3}, and it is likely that some of the remaining organic compounds did not undergo further decomposition. The coexistence of $HCO_3{}^-$ and CO_2 in the water appears to control the efficiency of UV ozone oxidation, because $HCO_3{}^-$ and CO_2 are thought to inhibit radical chain reactions.[17,18]

$$HCO_3{}^- + (OH)^\bullet \rightarrow CO_3 + H_2O. \quad (15)$$

After 2.0 h, the pH had decreased to a minimum 11.8. This is thought to occur due to the presence of low molecular organic acid and cyanate acids in the sample water. In this experiment, the concentration of COD decreased considerably during the treatment period. However, the concentrations of T-Fe remained constant during the entire experimental period and the concentration of T-CN decreased to a certain extent. In this experiment, residual T-CN seems to have been the CN^- ion that is contained in the iron-complex cyanides. After 0.5 h, the concentration of copper(II) ion decreased to an undetectable level. The hydroxyl radical is known to have a higher oxidation potential (2.85 V) than ozone (2.07 V).[19] These data suggest that the decomposition of iron-complex cyanides in wastewater is incomplete, despite the application of UV ozone oxidation. This method is therefore considered to be unsatisfactory for practical use.

Figure 5 depicts the results obtained following the UV ozone oxidation of wastewater samples. In this experiment, the wastewater samples were pre-processed, as shown in Fig. 3. In this experiment, T-CN in the pre-processed sample seemed to be remaining as free CN^- ion. The alkaline processed water (initial pH of 12.2) was circulated at a rate of 40 dm^3 h^{-1} with continuous filtration in the same manner as shown in Fig. 4. The total amount of ozone injected into the system was 540 mg h^{-1}. After the treatment, the concentration of cyanate ions began to increase along with a decrease in the T-CN (free CN^-), copper ion, COD, and pH values. After 30 min, T-CN (free CN^-) in the wastewater decreased to an undetectable concentration, and the concentration of cyanate ion reached a maximum value of 23 mg dm^{-3}. This is supposedly due to cyanate ion produced by the oxidation of cyanide ion, as follows:

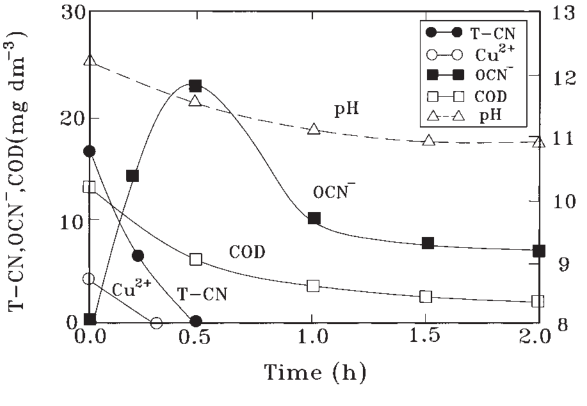

Fig. 5. Variations of T-CN, OCN^-, COD, and pH in UV ozone oxidation after treatment of UV photodecomposition using the iron-adsorbent.

$$CN^- + 2(OH)^\bullet \rightarrow OCN^- + H_2O \quad (16)$$

$$CN^- + O_3 \rightarrow OCN^- + O_2. \quad (17)$$

Furthermore, other radical species $(OOH)^\bullet$ are thought to exist in the aqueous phase, and to quickly oxidize the cyanide ion or organic matter:[20]

$$CN^- + 2(OOH)^\bullet \rightarrow OCN^- + H_2O + O_2. \quad (18)$$

Two hours later, the cyanate ion concentration had decreased to 7 mg dm^{-3}. In addition to the equilibrium discussed above, it is likely that some of the cyanate ion decomposed to $HCO_3{}^-$ and N_2 according to the following process:

$$2OCN^- + 6(OH)^\bullet \rightarrow 2HCO_3{}^- + N_2 + 2H_2O \quad (19)$$

$$2OCN^- + 3O_3 + H_2O \rightarrow 2HCO_3{}^- + N_2 + 3O_2 \quad (20)$$

$$2OCN^- + 2(OOH)^\bullet \rightarrow 2HCO_3{}^- + N_2. \quad (21)$$

These changes are considered to overlap with each other, and appeared to be slower reactions than the oxidation speed of cyanide ions, as shown in Eqs. 16, 17, and 18.

The results of this experiment therefore suggest that the decomposition of cyanate ion is a slow process requiring more than 2.0 h to reach completion. After two hours, the COD concentration was found to be 3.0 mg dm^{-3}. This value was probably due to the presence of organic compounds that had not undergone complete decomposition. After 2.0 h, the pH had decreased to a minimum of 10.9. This is thought to occur due to the organic and cyanic acids generated by the oxidation of wastewater. In summary, this method was not useful for the efficient removal of cyanide from wastewater. However, we then investigated the possibility of using a treatment process that combined the experiments described in Figs. 3 and 5. The removal of T-Fe takes place in the first 20 min of the treatment, as shown in Fig. 3. However, the removal of T-CN (free CN^-), copper(II), and COD clearly requires much longer treatment times. This method was effective to eliminate the T-Fe, but it was unsuitable to process T-CN (free CN^-), COD, and copper. On the other hand, the result shown in Fig. 5 indicate that T-CN (free CN^-) could be oxidized to OCN^- in a short time. Therefore, if combining the treatment process of Fig. 3 and Fig. 5, the decomposition of iron-complex cyanides and oxidation of T-CN (free CN^-) are thought to proceed effectively. This combined process was found to be suitable for pre-processing using the ion-exchange resin method, because the process affects the decomposition of iron-complex cyanides and oxidation of cyanide ion without requiring the addition of chemicals. Although the cyanide ion in the T-CN required short oxidation times, as shown in Fig. 5, the decomposition of cyanate ion required much longer processing times (over 2.0 h). We therefore applied a relatively brief oxidation time (up to 0.5 h) to facilitate the oxidation of cyanide ion into cyanate ion. The cyanate ion was then removed by passing the oxidized water through a cascade of ion-exchange resin columns. Since the use of UV ozone oxidation over extended time periods caused oxidative damage to ion exchange resins, we applied oxidation only over a short time period. The deionization of wastewater containing the iron-complex cyanides using singly the ion exchange resin could be applied over short time periods. However, when the iron-complex cyanides were contacted directly to an ion-exchange resin for extended time periods, they coated the surface of the resin and rapidly decreased the efficiency of ion exchange. Clearly, the combined process described in Figs. 3 and 5 seems to be suitable for the pre-processing of an ion-exchange resin method.

Table 1 presents the analytical results of wastewater samples Nos. 1 to 3 (the solution photodecomposed by UV irradiation using the iron-adsorbent at the alkaline side under the condition of ozone injection (60 $\mathrm{mg\,h^{-1}}$) for 60 min; the solution oxidized by ozone (total quantity of injected ozone, 540 $\mathrm{mg\,h^{-1}}$) combined with UV irradiation for 2.0 h; and the initial effluents from the cation resin column and anion resin column). The cyanate ion concentration at the outlet of the cation resin column was reduced to less than 1.5 $\mathrm{mg\,dm^{-3}}$. This is thought to have occurred due to the following processes in the cation resin column. Initially, neutral sodium cyanate was acidified in the cation resin column by the H-type cation resin. The cyanate ions were then converted into $\mathrm{NH_4}^+$ and $\mathrm{CO_2}$ by hydrolysis. The ammonium ions were then adsorbed by the cation resin. The process can be summarized as follows:

$$\mathrm{R{-}SO_3H + NaOCN \rightarrow R{-}SO_3Na + H^+ + OCN^-} \quad (22)$$

$$\mathrm{OCN^- + 2H^+ + H_2O \rightarrow NH_4{}^+ + CO_2} \quad (23)$$

$$\mathrm{R{-}SO_3H + NH_4{}^+ \rightarrow R{-}SO_3\ (NH_4) + H^+}. \quad (24)$$

The electrical conductivity of the effluent from the anion resin was less than 0.2 $\mathrm{mS\,m^{-1}}$. The concentrations of T-CN, T-Fe, copper, and cyanate ion in the effluent were below the detection levels. The COD concentration in the effluent from the anion resin column was less than 0.8 $\mathrm{mg\,dm^{-3}}$. This low COD concentration is thought to be due to adsorption of HCOOH by the anion-exchange resin as follows:

$$\mathrm{R{-}N{-}OH + HCOOH \rightarrow R{-}N{-}COOH + H_2O}. \quad (25)$$

Figure 6 depicts the relationship between the electrical conductivity of the effluent from the anion-exchange column (after passage through the cation resin column) and the treated water volumes of sample Nos. 1 to 3. A comparison was made between the pre-processed wastewater (UV photodecomposition for 60 min followed by UV ozone oxidation for 30 min) and the water without pre-processing. The electrical conductivity of the pre-processed water increased to a level similar to that of the treated water volume (between 53 and 67 $\mathrm{dm^3\,dm^{-3}}$-resin). However, the electrical conductivity of the water without pre-processing rapidly increased to the level of that of the treated water volume (between 5 and 8 $\mathrm{dm^3\,dm^{-3}}$-resin). These results indicate that the pre-processed water was deionized to less than 0.20 $\mathrm{mS\,m^{-1}}$, and that the de-ionized water could be recovered at a rate of 53 to 67-times that of the ion-exchange resin volume. Saturated ion exchange resins are easily regenerated. This de-ionized water can be reused as rinsing water in the plating processes.

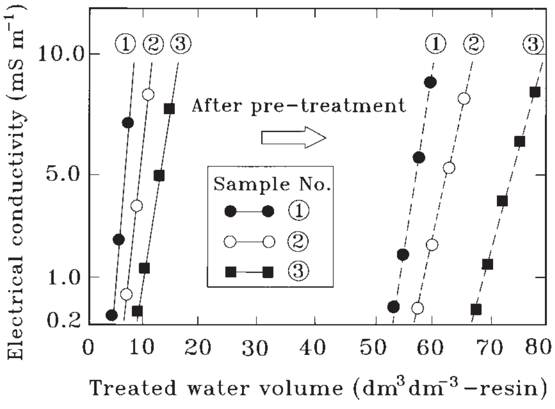

Fig. 6. Electric conductivity of the effluent from the ion-exchange resin column.

Conclusion

Iron-complex cyanides in alkaline wastewater were decomposed to iron and cyanide ($\mathrm{CN^-}$) ion by UV photodecomposition. The iron ion was removed by circulating the wastewater through an iron-adsorbent column under the condition of ozone injection. The UV ozone oxidation facilitated the rapid conversion of $\mathrm{CN^-}$ ion into $\mathrm{OCN^-}$ ion, and did not require the addition of chemicals. Passing the oxidized water through both cation and anion ion exchange columns resulted in the production of deionized water that could be recycled as rinsing water in the plating processes. The results reported here suggest that the combined three-process treatment (UV photodecomposition, UV ozone oxidation, and ion exchange resin method), as shown in Fig. 1, is a practical method for recycling wastewater contaminated with iron-complex cyanides without requiring the addition of chemicals.

References

1 G. Sam Samdani, *Chem. Eng.*, **101**, 17 (1994).

2 B. D. Petrides, C. Siletti, and J. Calandranis, *Ultrapure Water*, **19**, 26 (2002).

3 T. Yokomaku, *Hyomen Gijutsu (J. Surf. Finish. Soc. Jpn.)*, **48**, 261 (1997).

4 T. Kobayashi and K. Takahashi, *Yosui to Haisui (J. Water Waste)*, **7**, 660 (1965).

5 H. Honma, H. Mitsui, and H. Abe, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)*, **1977**, 1400.

6 H. Wada, *Hyomen Gijutsu (J. Surf. Finish. Soc. Jpn.)*, **48**, 1091 (1997).

7 S. Ohno, *Bull. Chem. Soc. Jpn.*, **40**, 1765 (1967).

8 S. Ohno, *Bull. Chem. Soc. Jpn.*, **40**, 1770 (1967).

9 S. Yamasaki, Y. Kisaki, and H. Ohura, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)*, **1990**, 682.

10 Y. Kosaka, *Hyomen Gijutsu (J. Surf. Finish. Soc. Jpn.)*, **48**, 243 (1997).

11 H. Wada and Y. Kuroda, *Hyomen Gijutsu (J. Surf. Finish. Soc. Jpn.)*, **50**, 1118 (1999).

12 H. Wada, T. Naoi, and Y. Kuroda, *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)*, **1994**, 834.

13 H. Hidaka, J. Zhao, and K. Nohara, *Yosui to Haisui (J. Water Waste)*, **36**, 863 (1994).

14 H. Hidaka, J. Zhao, and E. Pelizzetti, *J. Phys. Chem.*, **96**, 2226 (1992).

15 Y. Ogata, K. Tomizawa, and K. Fujii, *Bull. Chem. Soc. Jpn.*, **51**, 2628 (1978).

16 Y. Ogata, K. Tomizawa, and K. Takagi, *Can. J. Chem.*, **59**, 14 (1981).

17 J. Staehelin and J. Hoigne, *Water Res.*, **19**, 1206 (1985).

18 K. Kosaka, H. Yamada, K. Shishida, and S. Matsui, *J. Jpn. Soc. Water Environ.*, **22**, 888 (1999).

19 W. H. Glaze, J. W. Kang, and D. H. Chapin, *Ozone: Sci. Eng.*, **9**, 335 (1987).

20 A. Toyoda, L. Zhang, T. Kanki, and N. Sano, *J. Chem. Eng. Jpn.*, **33**, 188 (2000).