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Recycling of Cyanide Wastewater Applying Combined UV–Ozone Oxidation with a Titanium Dioxide Catalyst and Ion Exchange Resin Method

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We investigated how to reuse water from cyanide wastewater by combining UV–ozone oxidation with a titanium dioxide (TiO_2) catalyst and de-ionization by applying an ion exchange resin method. A TiO_2 catalytic film was formed on the surface of quartz tubes by a novel sol-gel method. During UV–ozone oxidation with the TiO_2 catalyst, cyanide ion (CN^-) was oxidized to cyanate ion (OCN^-) in a relatively short time without the application of any other chemicals. The processed water was smoothly de-ionized by an ion exchange resin method. The cyanate ion was decomposed into NH_4^+ and CO_2 by hydrolysis under acidic conditions in a cation exchange resin column. Ammonium ion (NH_4^+) adsorbed to the cation exchange resin. The electric conductivity of the effluent from the ion exchange resin column was less than 1×10^{-1} mS m^{-1}. This de-ionized water could be reused as rinsing water in the plating process. These experimental results suggested that toxic cyanide wastewater could be reused as de-ionized water.

In recent years, there has been increasing interest in purifying water without using chemicals to enable the recycling of wastewater.[1] Photocatalytic oxidation using a TiO_2 catalyst has attracted much attention concerning its highly effective photocatalytic function of decomposing many organic contaminations in the environment,[2,3] since it is reported that water can be decomposed photochemically.[4,5]

In order to practically implement water recycling from cyanide wastewater, we performed combined UV–ozone oxidation using a TiO_2 catalyst and the ion exchange resin method. The TiO_2 film functioned as a photo catalyst and was formed on the surface of quartz tubes using the sol–gel method.[6,7] To improve the method of immobilizing the TiO_2 film, we investigated a new composition of sol liquid. The quartz tube was used as a carrier of the catalyst. It was dipped into the sol liquid and pulled up slowly. The TiO_2 film on the quartz tube was dried at 403K and then heated at 823 K. We examined the photo-activity of this catalyst by measuring the de-colorization rate of a Methylene Blue (MB) solution by ozone oxidation combined with UV irradiation.

During oxidation, cyanide ion was quickly oxidized to cyanate ion without the addition of any other chemicals. The advantage of this oxidation process is that, unlike the conventional chlorination method,[8] it does not produce salts or chloride, which would have to be removed later to recycle the water.[9]

The oxidized water was passed through a cation exchange resin and an anion exchange resin, and then a mixed ion exchange resin column in that order. During a treatment by a cation exchange resin, the sodium ion of sodium cyanate was replaced by H^+, the cyanate ion was decomposed into NH_4^+ and CO_2 by hydrolysis under acidic conditions, and the ammonium ion was adsorbed onto the cation exchange resin. The electric conductivity of the effluent from the mixed ion exchange resin column was less than 1×10^{-1} mS m^{-1}, and no cyanide or cyanide ion was detected in the effluent. This de-ionized water could be reused as rinsing water without any other treatment in the plating processes.

In this paper, we report on the results of experiments regarding the oxidation of cyanide wastewater by using combined UV–ozone oxidation with a TiO_2 catalyst 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 TiO_2 catalytic film or copper(II) oxide were recorded using a Philips Model APD1700 X-ray diffractometer. The atomic-absorption data of metal ions were measured on a Nippon Jarrel-Ash (Model AA-880) atomic-absorption spectrophotometer. A Shimadzu spectrophotometer (Model UV-1240) was used to measure the absorption of on MB solution and ammonium ions. The ozone concentration was measured using an Ebara (Model EG-2001R) ozone monitor. The pH and electric conductivity were measured with digital pH and electric conductivity meters.

Analytical Methods: Cyanide ion, copper ion(II), COD and pH were measured according to JIS K0101 or JIS K0102. Cyanate ion was analyzed and found to be ammonium ion by the JIS K0102 indophenol-blue method after the hydrolysis of cyanate ion into ammonium ion by sulfuric acid.

Preparation of Photo Catalyst: A thin-filmed photocatalytic of TiO_2 was formed by an improved sol-gel method. The sol liquid was prepared by mixing titanium tetrabutoxide ($Ti(C_4H_9O)_4$), 86×10^{-3} mol of butyl alcohol [$CH_3(CH_2)_2CH_2OH$], 1 mol of isopropyl alcohol [$(CH_3)_2CHOH$] and 12×10^{-2} mol of

Table 1. Composition of Raw and Treated Water

Processing stage	Sample No.	pH	EC (mS m^{-1})	CN^-	OCN^-	Cu^{2+}	COD
				mg dm^{-3}			
Raw wastewater	1	10.3	65	110	0.0	21.5	25.0
	2	9.8	50	90	0.0	15.6	18.8
	3	10.5	55	105	0.0	18.5	20.3
Oxidized water by UV–ozone oxidation with TiO_2 catalyst (15 min)	1	8.5	67	0.1	163.2	0.3	3.6
	2	8.3	53	0.0	133.5	0.2	2.8
	3	8.9	58	0.0	156.2	0.2	3.2
Effluent of cation resin column	1	3.2	68	0.0	3.6	0.0	3.4
	2	3.4	55	0.0	2.5	0.0	2.5
	3	3.1	60	0.0	2.9	0.0	3.0
Effluent of anion resin column	1	8.6	1.5	0.0	0.0	0.0	0.8
	2	8.4	1.0	0.0	0.0	0.0	0.6
	3	8.5	1.3	0.0	0.0	0.0	0.9
Effluent of mixed resin column	1	7.3	0.08	0.0	0.0	0.0	0.6
	2	7.1	0.05	0.0	0.0	0.0	0.4
	3	7.2	0.06	0.0	0.0	0.0	0.5

2, 2′-iminodiethanol [$HN(CH_2CH_2OH)_2$] at a rate of 7×10^{-2} mol. A quartz tube serving as the carrier of the TiO_2 catalyst was dipped into the sol liquid for 5 minutes after cleaning by acetone, and then pulled from the sol liquid at 1.5 cm min^{-1}. The TiO_2 film on the quartz tube was dried in air at ambient temperature for 30 minutes, and then dried by heating at 403 K for 10 minutes, followed by final heating over a temperature range of 823 to 973 K for 20 minutes. The crystal form of the TiO_2 film was confirmed by X-ray diffractometry.

Samples: Cyanide plating was performed with copper, zinc, gold and silver. Since copper cyanide plating provides good adherence between the plating layer and the metal surface, it is introduced into the first stage of almost all plating processes. Therefore, a plating plant usually discharges copper(II) cyanide wastewater.

Wastewater from the copper(II) cyanide plating process generally contains alkaline chemicals (KOH, Na_2CO_3), copper cyanide (CuCN), sodium cyanide (NaCN) and organic matter such as tartaric acid $[CH(OH)COOH]_2$ or surfactant.[10] For example, the components of raw wastewater are shown Table 1 (samples No. 1 through No. 3).

Experimental Apparatus: Figure 1 shows a schematic diagram of the experimental apparatus. Cyanide wastewater from a raw water tank (1.0 dm^3) was filtered through a 5 μm filter, and then sent by a constant-rate pump (40 dm^3 h^{-1}) to an oxidation reactor. The reactor (3.0 dm^3) was equipped with a 40 w low-pressure mercury-vapor lamp that emitted UV rays (254 nm and 185 nm).

Part of the air sent to cool the lamp (at a rate of 2.0 dm^3 min^{-1}) was converted into ozone concentrated at 0.5 mg dm^{-3} due to UV rays of 185nm wavelength. This ozonized air was used efficiently for recycling by bubbling through the bottom of the reactor to oxidize the sample water.

Moreover, ozone from another portable ozone generator (generated at a concentration of 2.5 mg dm^{-3}) was distributed from the bottom of the reactor at a rate of 4.0 dm^3 min^{-1}. Treated water was sampled at the desired time interval and measured after being filtered through No. 5C filter paper. This portable generator produces ozone from the air. It uses the PSA method to reduce NO_x by-products by letting zeolite adsorb nitrogen in the air so as to bring the ozone concentration to more than 92%. The 140 quartz tubes coated with TiO_2 catalytic film (coated five times; outer diameter 5.5 mm, inner diameter 5.0 mm, and length 20 cm) are piled in two layers in the reactor.

In one experiment, all or part of the processed water was returned to a raw water tank. In another, all of the water flowed into a storage tank (1.0 dm^3). The processed water from the storage tank was filtered through a 5 μm filter to remove any metal sludge or other particles, and then flowed through three 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 was filled with a porous cation resin of the strong-acid type (H-type). The second ion-exchange column was filled with a porous anion resin of the strong-alkaline type (OH-type), and the third ion-exchange column was filled with a mixed H-type cation resin and OH-type anion resin at a ratio of 1:2 in volume.

The water processed by UV–ozone oxidation using the TiO_2 catalyst was sent through the ion exchange resin column at a rate of 10 dm^3 dm^{-3}-resin/h (10 space velocity, SV10 hereafter). The treated water was sampled from the drains of each resin column at the desired time interval. The amount of absorbed components per unit volume of resin was calculated from the treated water volume (the water volume of dm^3 passed through 1 dm^3 of total resin volume), when the electrical conductivity of the effluent rapidly increased.

Result and Discussion

Figure 2 shows the X-ray diffraction patterns of the TiO_2 catalytic film at various coating temperatures. The coating of TiO_2 film was repeated five times for each dipping and heating. The crystalline structure of the TiO_2 film that was merely heated to 403 K for 10 minutes cannot be clearly identified. This film appeared to be an amorphous precipitate of TiO_2. When the film was dried at 403 K for 10 minutes, followed by contin-

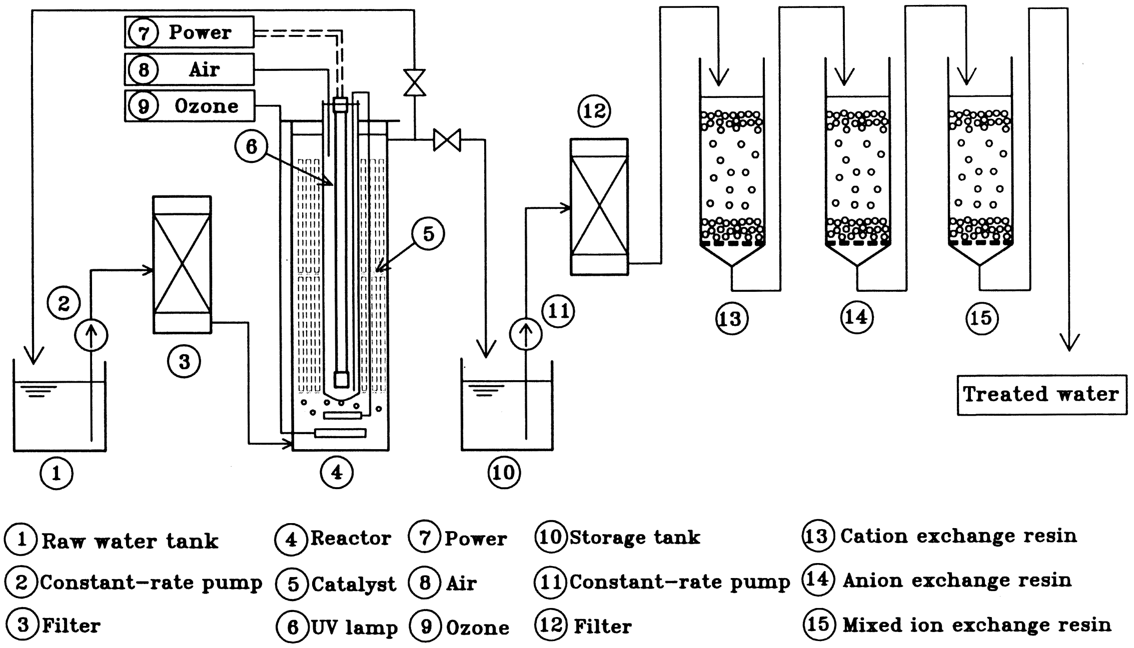

Fig. 1. Schematic diagram of the apparatus to treat cyanide wastewater applying combined UV–ozone oxidation with a TiO_2 catalyst and ion exchange method.

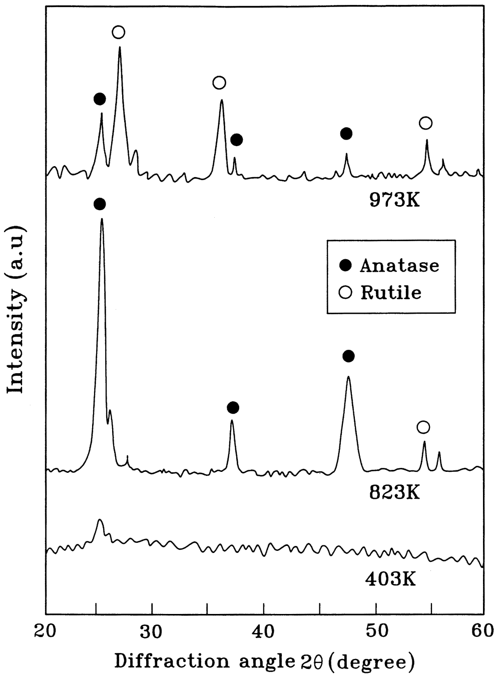

Fig. 2. X-ray analysis of TiO_2 catalytic film at various coating temperatures.

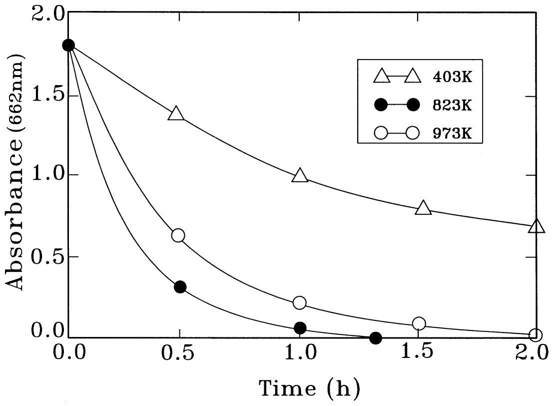

Fig. 3. Time course changes of absorbance at 662 nm of the MB solution at various coating temperatures of TiO_2 catalytic film.

uous heating at 823 K for 20 minutes, it exhibited a strong anatase crystal peak and a weak rutile crystal peak. In contrast, the film dried at 403 K for 10 minutes and heated at 973 K for 20 minutes exhibited a strong rutile crystal peak and a weak anatase crystal peak. This indicated that most of the thin-film photo catalyst of TiO_2 was converted from anatase crystal to rutile crystal. We investigated the photo-activity of the TiO_2 catalyst by irradiating it with 254 nm UV light in a Methylene Blue (MB) solution, and measured the effect of de-colorization for the MB solution by measuring the absorption spectra.

Figure 3 shows the time-course changes of the absorbance at 662 nm of the MB solution (10 mg dm^{-3}) and various coating temperatures of the TiO_2 film. The maximum absorption peak of the MB solution was observed at a wavelength of 662 nm. The effect of de-colorization of the MB solution was examined by UV–ozone (60 mg h^{-1}) oxidation using a TiO_2 catalyst. A small amount of ozone (generated by the UV lamp at a concentration of 0.5 mg dm^{-3}) was bubbled through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1}. This experiment was carried out batch-wise.

The TiO_2 catalytic film that was applied at 823 K tended to decrease in absorbance of the MB solution compared to other TiO_2 catalytic films that were formed at 403 K and 973 K. This indicated that the anatase-type TiO_2 film on the quartz

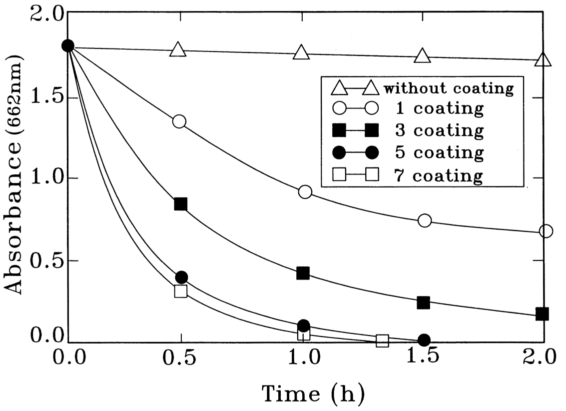

Fig. 4. Time course changes of absorbance at 662 nm of the MB solution at various coating times of TiO_2 catalytic film at 823 K.

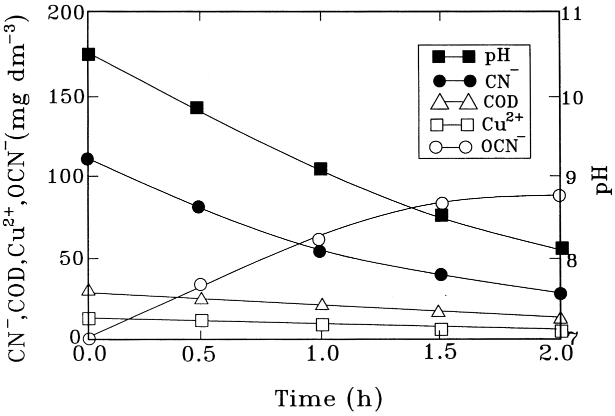

Fig. 5. Variations of CN^-, COD, Cu^{2+}, OCN^- and pH in UV–ozone (60 mg h^{-1}) oxidation combined with the TiO_2 catalyst.

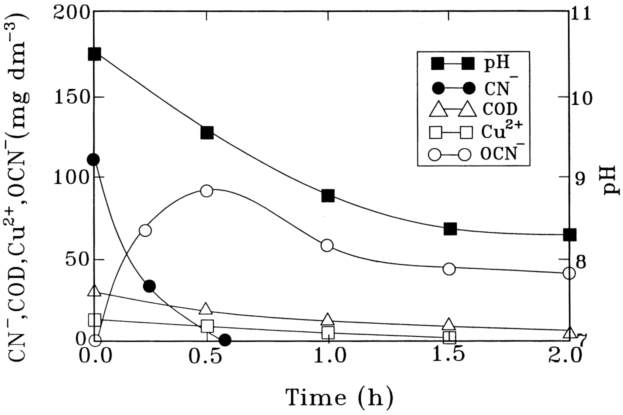

Fig. 6. Variations of CN^-, COD, Cu^{2+}, OCN^- and pH in UV–ozone (660 mg h^{-1}) oxidation without using the TiO_2 catalyst.

tubes yielded effective photocatalytic results. The anatase-type TiO_2 film indicates a higher oxidation potential (3.2 V) than the rutile type (3.0 V).[11] From these experiments, we adopted drying at 403 K for 10 minutes then heating to 823 K for 20 minutes, because this process appeared to produce the anatase TiO_2 crystal on the quartz most effectively.

Figure 4 shows time-course changes of the absorbance at 662 nm of the MB solution (10 mg dm^{-3}) and various coating times of TiO_2 film at 823 K. This experiment was conducted in the same manner as that shown in Fig. 3. The tendency of the MB solution absorbance to decrease was accelerated as the coating times increased, but the rates for five coatings and seven coatings were almost the same. These data seem to suggest that the coating times influence the rate at which the MB solution absorbance decreases. When the number of coatings exceeds a specific number, the rate of decrease in the MB solution absorbance becomes constant. Consequently, five coatings are thought to be adequate for de-colorizing the MB solution.

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

Figure 5 shows the experimental result of UV–ozone (60 mg h^{-1}) oxidation combined with the TiO_2 catalyst for a raw wastewater sample (No. 3 in Table 1). A rarefied concentration of 0.5 mg dm^{-3} of ozone generated by the UV lamp was bubbled through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1}. Ozone was thus injected at a combined rate of 60 mg h^{-1}. All of the processed water was circulated at a rate of 40 dm^3 h^{-1} from the raw water tank through the filter and the reactor and back to the raw water tank.

The concentration of cyanate ion began to rise as the pH, cyanide ion, COD and copper(II) ion decreased. Various elementary reactions are thought to occur in series or parallel on the surface of TiO_2. The UV irradiation of the TiO_2 photo catalyst in the water appeared to form positive holes (p^+) and electrons (e^-), after which water was decomposed into oxygen and hydrogen.[5] At the same time, hydroxyl radicals $(OH)^\bullet$ were generated on the surface of illuminated TiO_2 by the reaction of positive holes (p^+) with water molecules or hydroxide ions.[12–14]

$$TiO_2 + 2h\nu \rightarrow 2p^+ + 2e^- \quad (1)$$

$$2p^+ + H_2O \rightarrow 1/2O_2 + 2H^+ \quad (2)$$

$$p^+ + H_2O \rightarrow (OH)^\bullet + H^+ \quad (3)$$

$$p^+ + OH \rightarrow (OH)^\bullet \quad (4)$$

After 2.0 hours, cyanate ion increased to 80 mg dm^{-3}. This is supposedly due to cyanate ion produced by the oxidation of cyanide ions as follows.

$$CN^- + 2(OH)^\bullet \rightarrow OCN^- + H_2O \quad (5)$$

Some cyanide ions are probably oxidized by ozone to cyanate ions.

$$CN^- + O_3 \rightarrow OCN^- + O_2 \quad (6)$$

The hydroxyl radical indicates a higher oxidation potential (2.85 V) than does ozone (2.07).[15] However, this process appeared to be insufficient in the oxidation effect because of a shortage of ozone supply. Two hours later, although the number of cyanide ions decreased to 30 mg dm^{-3}, some cyanide ions still remained in the wastewater. This suggests that UV photo-oxidation combined with the use of the TiO_2 catalyst with the bubbling of a small amount of ozone (60 mg h^{-1}) may require additional oxidation time. This method is probably unsatisfactory for practical use.

Figure 6 shows the experimental result of UV–ozone (660 mg h^{-1}) oxidation without using the TiO_2 catalyst for raw wastewater sample No. 3 in Table 1. Wastewater was circulated at a rate of 40 dm^3 h^{-1} with continuous filtration. Ozone from the ozone generator (generated at a concentration of 2.5 mg dm^{-3}) was distributed through the bottom of the reactor at a rate of 4.0 dm^3 min^{-1} to oxidize the wastewater. A rarefied concentration of 0.5 mg dm^{-3} of ozone generated by the UV lamp also bubbled through the bottom of the reactor at a rate of 2.0 dm^3 min^{-1}. Therefore, the total amount of ozone injected was 660 mg h^{-1}.

The concentration of cyanate ion began to rise as the amount of pH, cyanide ion, COD and copper(II) ion decreased. After 30 minutes, the concentration of cyanate ions reached a maximum value (100 mg dm^{-3}) and then gradually decreased to 45 mg dm^{-3}. The cyanide ion decreased to an undetectable level simultaneously. Additional hydroxyl radical $(OH)^{\bullet}$ is thought to be generated individually by a sufficient amount of ozone and the 254 nm of UV in the water.[16]

$$O_3 + h\nu \rightarrow [O] + O_2 \tag{7}$$

$$[O] + H_2O \rightarrow 2(OH)^{\bullet} \tag{8}$$

This hydroxyl radical $(OH)^{\bullet}$ appeared to further accelerate the oxidation speed of cyanide or organic matter. Furthermore, another radical species $(OOH)^{\bullet}$ is thought to be generated by O_2 and electron (e^-) in the water.[17,18]

$$O_2 + e^- \rightarrow O_2^- \tag{9}$$

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

$$CN^- + 2(OOH)^{\bullet} \rightarrow OCN^- + H_2O + O_2 \tag{11}$$

Those radical species [$(OH)^{\bullet}$ or $(OOH)^{\bullet}$] are thought to exist in the aqueous phase and to quickly attack the cyanide ion or organic matter.[19] In addition to the equilibrium discussed above, some cyanate ions are thought to be decomposed to HCO_3^- and N_2 as follows.

$$2\,OCN^- + (OH)^{\bullet} + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2 \tag{12}$$

$$2\,OCN^- + 2(OOH)^{\bullet} \rightarrow 2HCO_3^- + N_2 \tag{13}$$

$$2\,OCN^- + 3O_3 + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2 \tag{14}$$

These changes are considered to overlap each other and appeared to be slower reactions than the oxidation speed of cyanide ions by Eqs. 5, 6, and 11. This experiment suggests that the decomposition of cyanide is still incomplete after more than 2.0 hours. This method also seems to be unsatisfactory for practical use.

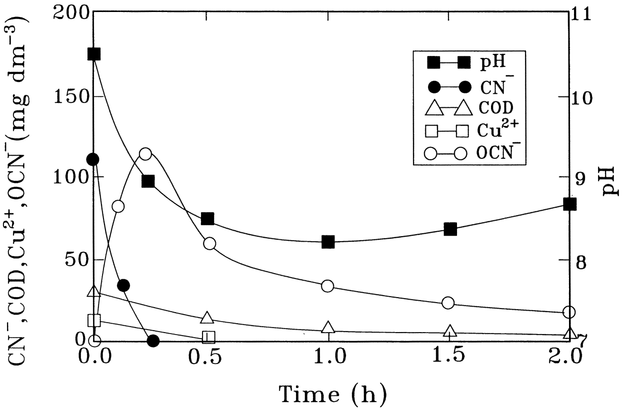

Fig. 7. Variations of CN^-, COD, Cu^{2+}, OCN^- and pH in UV–ozone (660 mg h^{-1}) oxidation combined with the TiO_2 catalyst.

Figure 7 shows the experimental result of UV–ozone (660 mg h^{-1}) oxidation combined with using the TiO_2 catalyst for raw wastewater sample No. 3 in Table 1. This experiment was conducted in the same manner as that in Fig. 6 using the TiO_2 catalyst. The total injected ozone rate was of 660 mg h^{-1}. Raw water was circulated at a rate of 40 dm^3 h^{-1} with continuous filtration.

The concentration of cyanate ion began to rise as the cyanide ion, copper(II) ion, pH and COD decreased. After 15 minutes, cyanide ion decreased to an undetectable level. At the same time, the concentration of cyanate ion reached a maximum value of 120 mg dm^{-3}. These changes are thought to be due to cyanate ion produced by the oxidation of cyanide ion by multiple reactions, as in Eqs. 5, 6 and 11. After 30 minutes, the concentration of copper ion(II) decreased to an undetectable level, and a blue metal sludge emerged from the processed water simultaneously. After 1.0 hour, this sludge changed to brown-colored crystals, which were identified as being copper(II) oxide (CuO) by X-ray diffractometry.

This is thought to occur due to the following processes in the reactor. First, tetracyanocuprate(II) ion is oxidized by the $(OH)^{\bullet}$ radicals, and transformed into blue copper(II) hydroxide [$Cu(OH)_2$].

$$[Cu(CN)_4]^{2-} + 10(OH)^{\bullet} \rightarrow Cu(OH)_2 + 4\,OCN^- + 4H_2O \tag{15}$$

Next, the copper(II) hydroxide is transformed into copper(II) oxide due to further oxidation of the $(OH)^{\bullet}$ radical as follows.

$$Cu(OH)_2 + (OH)^{\bullet} \rightarrow CuO + H_2O + OH^- \tag{16}$$

It was shown that UV–ozone (660 mg h^{-1}) oxidation combined with using the TiO_2 photo catalyst was much more effective than the oxidation method without using the TiO_2 catalyst. The reaction rate of cyanide ion was twice as fast as oxidation without using the TiO_2 catalyst. This was probably due to the synergistic effect of UV, ozone (quantity of 660 mg h^{-1}), oxygen and TiO_2 catalyst. After 15 minutes, the concentration of cyanate ion increased to the maximum value (120 mg dm^{-3}), and then fell quickly, followed by gradual reduction to 20 mg dm^{-3} 2.0 hours later. These changes are considered to be due to the same decomposition of cyanate ion as in Eqs. 12 through 14. This experiment suggests that the decomposition of cyanate ion is still incomplete after more than 2.0 hours.

One hour later, the COD was less than 5.0 mg dm^{-3} due to the oxidation effects of the COD components, such as tartaric acid or a surfactant as additive chemicals.[10] Those COD components appeared to be finally decomposing to CO_2 and H_2O through some organic acids. For example, tartaric acid was finally decomposed to CO_2 and H_2O as follows.[20]

$$[CH(OH)COOH]_2 + 2(OH)^\bullet \rightarrow [CH(OH)_2COOH]_2 \quad (17)$$

$$[CH(OH)_2COOH]_2 + h\nu \rightarrow 2HOCCOOH + H_2O \quad (18)$$

$$HOCCOOH + 2(OH)^\bullet \rightarrow HCOOH + CO_2 + H_2O \quad (19)$$

$$HCOOH + 2(OH)^\bullet \rightarrow CO_2 + H_2O \quad (20)$$

Two hours later, the COD level was still 3.0 mg dm^{-3}, probably due to some remaining organic compounds that had not undergone further decomposition. The coexistence of HCO_3^- or CO_2 in the water appears to control the efficiency of the UV–ozone oxidation with a TiO_2 catalyst,[21] because HCO_3^- or CO_2 are thought to inhibit radical chain reactions.[22]

$$HCO_3^- + (OH)^\bullet \rightarrow CO_3 + H_2O \quad (21)$$

One hour later, the pH value had decreased to the minimum 8.3, and then began rising. This is likely to be due to the organic matter being finally decomposed to CO_2 and H_2O through organic acid. Despite the short oxidation times of cyanide ions, because the decomposition of cyanate ion appeared to require over 2.0 hours, we chose brief oxidation times of up to 15 minutes (until cyanide ion was oxidized into cyanate ion).

Since using a method with lengthy times of UV–ozone oxidation with a TiO_2 catalyst is not practical, and is supposed to cause oxidation damage to the ion exchange resin, we used the brief oxidation time described above. Furthermore, we also adopted highly cross-linked and porous ion exchange resin, which could withstand oxidation damage and contaminated water. We tried to remove cyanate ion by passing the oxidized water through a cascade of ion exchange resin columns. By directly treating cyanide wastewater by ion exchange resin for a short time, it may be possible to adsorb cyanide ion and make de-ionized water. However, if cyanides contact the H-type cation resin and are acidified in the cation resin vessel, the cyanides are changed into harmful cyanogens gas, and the efficiency of the reaction by an ion exchange reaction is quickly reduced. Therefore, the decomposition of cyanide ion by ozone oxidation combined with UV irradiation and a TiO_2 catalyst before a treatment of the ion exchange resin may be useful for promoting on effective reaction of the ion exchange resin.

Table 1 shows the analysis results of raw wastewater samples No. 1 through 3; the solution oxidized by UV and ozone (total quantity of injected ozone, 660 mg h^{-1}) oxidation combined with a TiO_2 catalyst for 15 minutes; and the initial effluents from the cation resin column, anion resin column and mixed resin column.

The cyanate ion at the outlet of the cation resin column was reduced to less than 4 mg dm^{-3}. This is thought to have occurred due to the following schemes in the cation resin column.

First, neutral sodium cyanate was initially acidified in the cation resin column by the H-type cation resin and changed into cyanate ion; second, the cyanate ion was converted into NH_4^+ and CO_2 by hydrolysis; third, ammonium ion was adsorbed by the cation exchange resin as follows.

$$R–SO_3H + NaCNO \rightarrow R–SO_3Na + H^+ + OCN^- \quad (22)$$

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

$$R–SO_3H + NH_4^+ \rightarrow R–SO_3(NH_4^+) + H^+ \quad (24)$$

The electrical conductivity of the effluent from the mixed resin column was less than 0.1 mS m^{-1}. No cyanides, cyanate ion or copper ion were detected in the effluent. The COD of the effluent from the anion resin column was less than 1.0 mg dm^{-3}. This is assumed to be due to the effect of adsorption of the HCOOH by the anion exchange resin.

$$R–N–OH + HCOOH \rightarrow R–N–COOH + H_2O \quad (25)$$

Figure 8 shows the relation between the electrical conductivity of the effluent from the mixed ion exchange column (after passing through the cation resin column and the anion resin column) and the treated water volume of samples No. 1 through 3 after processing by UV–ozone oxidation combined with the TiO_2 catalyst for 15 minutes. The electrical conductivity began to increase to the level of that of the treated water volume, between 55 and 70 dm^3 dm^{-3}-resin. These results indicated that water de-ionized to less than 1×10^{-1} mS m^{-1}, and that the de-ionized water could recover at a rate of 55 through 70 times of the ion exchange resin volume.

This de-ionized water can be reused as rinsing water without any other treatment in the plating processes. Saturated ion exchange resins are easily regenerated. This process consider-

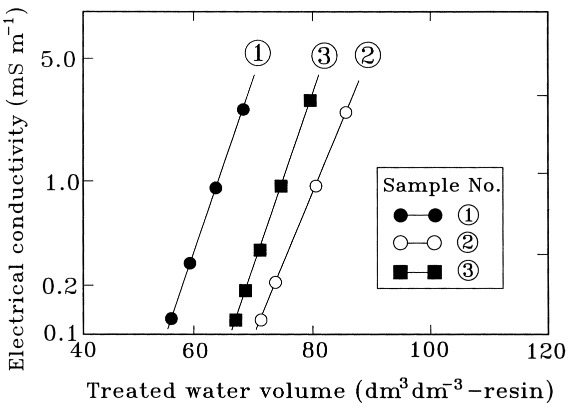

Fig. 8. Electric conductivity of the effluent from the mixed ion exchange resin column.

ably reduces the burden on the water environment and could possibly create economies in recycling wastewater.

Conclusion

Ozone oxidation employing UV irradiation combined with a TiO_2 catalyst can convert cyanide ion into cyanate ion in a short time without the addition of any other chemicals. Furthermore, by passing the oxidized water through cation, anion and then mixed ion exchanger columns, we can obtain high-purity de-ionized water that can be used as rinsing water in plating processes.

These results suggest that this process does not cause any secondary pollution, and has a high possibility of being practically applied for recycling water from cyanide wastewater.

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