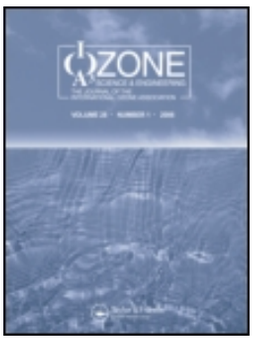

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Treatment of Jewelry Manufacturing Effluent Containing Cyanide Using Ozone-Based Photochemical Advanced Oxidation Processes

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This article considers Advanced Oxidation Processes involving O_3, O_3/UV, $O_3/H_2O_2/UV$, and H_2O_2/UV to destroy cyanide in jewelry manufacturing wastewaters. All experiments were performed in a semibatch reactor. The results showed that total cyanide can be reduced with different reaction rates, and the decrease of total cyanide can be described by pseudo–first-order kinetics. The reaction was performed under different pH values and H_2O_2 dosages to find the optimal conditions for the oxidation processes. The ozonation process destroyed total cyanide faster at a pH = 12, whereas ozonation combined with H_2O_2 and/or UV destroyed cyanide faster at a pH =10. The total cyanide destruction rate in the UV/H_2O_2 (700 mg/L*) treatment was the highest among all studied processes, with removal efficiencies of 99% for CN^-, 99% for COD and 99% for TOC.*

Keywords Ozone, Jewelry Manufacturing Effluent, Cyanide, Advanced Oxidation Processes, UV, H_2O_2

INTRODUCTION

Cyanide provides the basic structure for the organic compounds of the "cyano" group (Priyadarshan 2000). This compound is also a toxic pollutant in a multitude of wastewaters and must be degraded prior to discharge. Cyanide is produced globally at an annual rate of approximately 2–3 million tons, primarily consumed by industries such as mining (mainly extraction of gold), electroplating, case hardening, automobile manufacturing, circuit board printing, steel manufacturing, and chemical production. These industries discharge cyanide containing wastewaters (Patil and Paknikar 2000; The Mining Bulletin 1997).

Cyanide can be found in environmental matrices and waste streams as simple cyanides (e.g., HCN, CN, NaCN), metal cyanide complexes, cyanates and nitriles (Ebbs 2004). The most toxic form of cyanide is free cyanide, which includes the cyanide anion itself and hydrogen cyanide (HCN), either in a gaseous or aqueous state (Dash et al. 2009). Cyanide compounds found in industrial wastewaters are usually of species less toxic than HCN and cyanide, and their concentrations display a wide range of 0.01–10,000 mg/L. Cyanide has featured prominently for the past 100 years as a leach reagent at gold mines and secondary sources because of its high efficiency and relatively low cost, and more than 18% of all cyanide produced is used in mining operations around the world for recovering gold (Syed 2012). In Turkey, 1600 tons of cyanide are consumed in a year with 600 tons being consumed at the Etibank Silver Mine and 1000 tons being consumed by the plating industry and jewelry sector (The Mining Bulletin 1997). The global maximum discharge standard for cyanide is 0.01 mg/L in water and 5 mg/m^3 in air (Gümüş 1975). However, there is no specific total cyanide discharge limit for the jewelry sector in Turkey. Without appropriate treatment, toxic chemical contamination, including cyanides, can be harmful to living organisms (Patil and Paknikar 2000).

Conventional treatment methods to remove cyanide from wastewaters, which include biological oxidation/biodegradation, adsorption on activated carbon, chemical oxidation using caustic chlorination, oxidation with wet air, addition of hydrogen peroxide, application of the SO_2/air (INCO) process, ozonation, anodic oxidation, electrodialysis, reverse osmosis, electrowinning, hydrolysis/distillation, acidification/volatilization with re-neutralization, flotation, iron cyanide precipitation, application of a resin, catalytic

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oxidation, addition of Caro's acid and photolysis, all have certain drawbacks. Some of these methods may not destroy the pollutants completely, are currently not well established, and/or are not cost effective (Freeman 1989; Valsero et al. 2013). In the most commonly used method of applying caustic chlorine, cyanide is converted to the toxic and more recalcitrant cyanate. The chlorination process also produces secondary by-products such as the carcinogenic cyanogen chloride (Kosaku 1975).

Biological treatment with microorganisms that hydrolyze cyanide by a cyanase enzyme is also effective in destroying cyanide. Cyanide concentrations range between 2 to 50 mg/L in wastewater treatment plants. However, the total percent of cyanide decomposed never exceeded 36%. Furthermore, 2 mg/L of cyanide can inhibit nitrification. Nevertheless, bacteria can adapt to higher concentrations and have been shown to decompose 30 mg/L of cyanide (Roques 1996; Turan et al. 2003). Adsorption is a widely used technology for the removal and recovery of cyanide, and activated carbon is known to be effective for the oxidation of cyanide. However, activated carbon oxidizes cyanide to cyanate (Adams 1994).

Considering the disadvantages of conventional treatment methods, AOPs can be a good treatment alternative for the complete destruction of cyanide. Limited studies of AOPs used to remove cyanide from the effluent of the mining industry exist in the current literature (Kim et al. 2003) but we can find some studies for the treatment of cyanide for other industries. Monteagudo et al. (2004) made some experiments by using ozone or/and hydrogen peroxide or/and UV radiation in a mixed semi-batch buble reactor for the treatment of cyanide effluent from a thermoelectric power station. They had the best cyanide degradation rate in the O_3/H_2O_2 and the COD reduction was about 75% in the process using O_3UV, or O_3/H_2O_2/UV. Ford et al. (2005) used low-pressure Ultraviolet (LPUV) light/ozone (O_3), medium- pressure UV (MPUV)/hydrogenperoxide (H_2O_2), MPUV/O_3/H_2O_2, and peroxone (combination of O_3 and H_2O_2) for the treatment of cyanide contaminated wastewater from an engine manufacturing company and they have found that for CN and TOC removal MPUV/ozonation system and for CN removal alone MPUV/hydrogen peroxide system have given the best results. Kepa et al. (2008) made some laboratory tests and made some analyses by using the processes ozonation, oxidation with hydrogen peroxide, and advanced oxidation in the $O_3 + H_2O_2$ system.

They found that the highest effectiveness of cyanide removal with the oxidation methods used was achieved a by H_2O_2 + O_3 system. Mudliar et al. (2009) studied on the destruction of cyanide (CN) from an automobile industry wastewater by advance oxidation process (AOP). They found that a combined application of H_2O_2/O_3 was found to be the best option for maximum CN destruction. This treatment allows CN to reach the regional/international limit (of 0.02 mg/L) for safe industrial wastewater discharges to the receiving water bodies. Vohra (2011) studied on the removal of thiocyanate from synthetic wastewater using TiO_2 mediated photocatalytic degradation process.

TABLE 1. Characterization of Jewelry Manufacturing Effluent Wastewater

Parameter	Concentration
Total Cyanide	51 ± 4 mg/L
COD	65 ± 12 mg/L
TOC	18 ± 6 mg/L
pH	10–12

The aim of this study is to evaluate the total cyanide, COD, and TOC removal in jewelry manufacturing effluent, to find optimal operating conditions of the applied processes and establish the kinetics of the photochemical oxidation processes.

MATERIALS AND METHODS

Characterization of Jewelry Wastewater

Jewelry manufacturing wastewater samples were taken from a jewelry workshop in Bursa City, Turkey, which is the fourth most populous city in Turkey and one of the most industrialized metropolitan centers in the country. The characteristics of the jewelry manufacturing wastewater are displayed in Table 1.

Photochemical Reactor

The semibatch-mode photoreactor used in this study is shown in Figure 1. The lamp is a monochromatic (wavelength of 1 = 254 nm, UV-C energy) TUV-15 lamp (Phillips Lighting) with a nominal power of 15 W. The UV lamp was enclosed in a quartz sleeve with an inner diameter of 39 mm

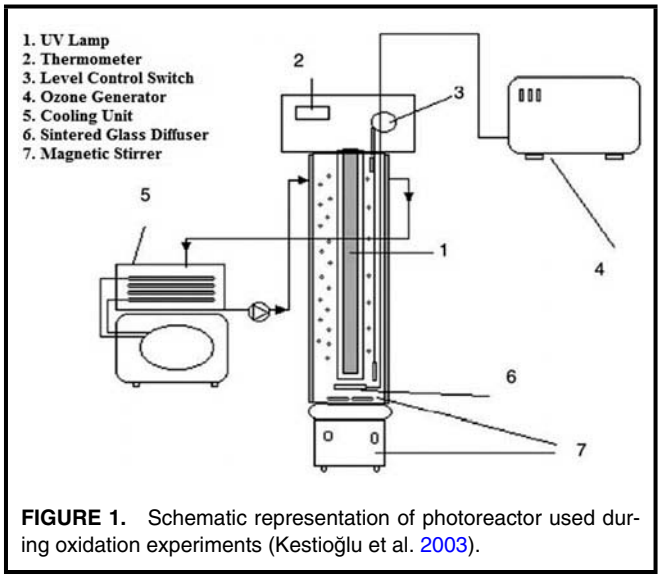

FIGURE 1. Schematic representation of photoreactor used during oxidation experiments (Kestioğlu et al. 2003).

and a length of 39 cm. The lamp was positioned within the center of a 2.8-L cylindrical stainless steel reactor. The body of the reactor was made of 316-Ti stainless steel with an inner diameter of 98 mm and a length of 41 cm. The light intensity along the axial length was measured by radiometry (3DCURE radiometer, EIT Inc., USA), and the 3-dimensional fluence rate (irradiance) distribution of the photoreactor was calculated by UVCalc 1.05 software (Bolton Photosciences Inc., Canada).

The average fluence rate was 0.68 mW/cm^2. A water jacket was installed around the reactor to keep it at a desired temperature (22 ± 0.5 °C) by a thermostat controlled continuous water recirculation system. The re-circulating cooling water and the wastewater sample never mixed. The content of the reactor (2.8 L) was continuously mixed by a magnetic stirrer.

Ozone (O_3) was generated by an Opal 200 model ozonizer, Turkey, fed by corona discharge with a maximum ozone (O_3) production of 0.208 g/h at 60 L/h air flow. The ozone generation unit was integrated into the reactor to produce the ozone (O_3) required during the O_3, O_3/UV and O_3/H_2O_2/UV experiments. The ozone (O_3) was bubbled into reactor by a sintered glass plate diffuser. The inlet and outlet of the reactor were directed to gas washing bottles filled with a 2% KI solution to determine the ozone concentration. The ozone concentration was measured by the iodometric method proposed by the IOA Standardization Committee (1987).

In all experiments, the ozone gas flow rate was set at 180 mg/h. Prior to testing, the pH was manually adjusted using sodium hydroxide (Merck), and was controlled throughout the experiment by a pH meter. Following the pH adjustment, a specified amount of H_2O_2 (Merck, 35% w/w) was added, and the lamp and ozone (O_3) generator was turned on. Following the determination of the optimal pH, identical experiments were performed at the optimal pH with varying H_2O_2 concentrations: 25–300 mg/L for the O_3/H_2O_2/UV experiments and 100–900 mg/L for the UV/H_2O_2 experiments.

ANALYTICAL PROCEDURE

The total cyanide concentration (mg CN^-/L, Standard Methods 4500 CN, APHA/AWWA/WEF 1998) was measured using the colorimetric method on a UV-Vis spectrophotometer (Hachlange, Model DR 5000, USA). The chemical oxygen demand (COD mg O_2/L) was determined by using the Dichromate Reflux Method (5220-C) in accordance with Standard Methods (APHA/AWWA/WEF 1998). TOC was determined using a Shimadzu-5050A TOC analyzer, Japan.

The pH was manually adjusted to desired range using sodium hydroxide (supplied from Merck) and was controlled throughout the experiments. Following the pH adjustment a specified amount of H_2O_2 (supplied from Merck, 35% w/w) was added, and the lamp and ozone (O_3) generator was turned on. Following the determination of optimum pH, same experiments were carried out at the optimum pH with varying H_2O_2 concentrations 25–300 mg/L for O_3/H_2O_2/UV experiments and 100–900 mg/L for UV/H_2O_2 experiments.

The samples containing H_2O_2, which interferes with COD measurements, was removed by adding MnO_2 powder (Arslan and Balcıoğlu 1999; Azbar et al. 2004). The concentration of residual hydrogen peroxide (H_2O_2) in the test solution was determined by using test strips (Merckoquant Peroxide Test, Merck Pharmaceuticals). Samples were taken at regular time intervals to determine concentrations of cyanide, COD, and TOC. For controlling pH we used phosphate (50 mM) Buffer.

RESULTS AND DISCUSSION

UV/H_2O_2 Experiments

Light can degrade many compounds by triggering bond cleavage in organic compounds, although with a slow degradation rate (Sarla et al. 2004). After 90 min of irradiation, Sarla et al. (2004) reported that 100 mg/L of cyanide degraded to 98 mg/L. However, when H_2O_2 was added in addition to UV, the rate of degradation was much faster. After 65 min, 100 mg/L of cyanide was completely degraded. Ultraviolet radiation in combination with H_2O_2 addition can create a fast and efficient process for water treatment by producing hydroxyl radicals as displayed in Equation [1]:

$$H_2O_2 + hv \rightarrow 2HO\bullet \quad [1]$$

The oxidation of cyanide by ($OH^\bullet$) is displayed below in Equation [2].

$$CN^- + 2HO\bullet \rightarrow OCN^- + H_2O \quad [2]$$

Previous investigations have confirmed that cyanate is formed (Augugliaro et al. 1997; Design Test Report 2003). Cyanate is then oxidized under continuous photolytic ozonation to produce bicarbonate and either nitrogen gas, nitrite or nitrate.

Young et al. (1995) reported that during cyanate oxidation, the formation of the end products (nitrite or nitrate) depends on the amount of excess H_2O_2 present during the reaction. As seen here:

$$OCN^- + 3\,HO\bullet \rightarrow HCO_3^- + {}^1\!/_2 N_2(g) + H_2O \quad [3]$$

$$OCN^- + 6\,HO\bullet \rightarrow HCO_3^- + NO_2^- + H^+ + 2H_2O \quad [4]$$

$$OCN^- + 8\,HO\bullet \rightarrow HCO_3^- + NO_3^- + H^+ + 3H_2O \quad [5]$$

If the pH is less than 7, cyanate can undergo natural hydrolysis and produce ammonium and bicarbonate ions. In this study, the photo-chemical oxidations were performed at an alkaline pH (10–12) preventing natural hydrolysis. This was confirmed by the end products being carbon dioxide and nitrogen. In numerous studies, acidic pH values (<3) are used

in UV/H_2O_2 processes (Rathi et al. 2003; Yonar et al. 2005). However, this study performed experiments at an alkaline pH to avoid producing highly toxic hydrogen cyanide gas. It is known from the earlier studies that (sodium) phosphate (50 mM) has no effect on the kinetics of the chain reaction cause of this pH was buffered by phosphate (Hoigne and Bader 1979).

Figure 2 displays the effect of pH on the removal of cyanide and COD when hydrogen peroxide was at a constant concentration of 100 mg/L. The cyanide and COD removal efficiencies increase as the pH decreases to 10. The resulting effluent cyanide, COD and TOC removal efficiencies were 99%, 96% and 97%, respectively. However, similar removal efficiencies of cyanide, COD, and TOC occurred at a pH of 11 or 12. After determining the optimal pH, the dosage of hydrogen peroxide was examined.

Hydrogen peroxide acts as an effective scavenger of hydroxyl radicals ($HO^{\bullet}$) at high concentrations. If H_2O_2 exceeds the optimum dose, less reactive hydroperoxyl radicals ($HO_2^{\bullet}$) are produced and excess $HO^{\bullet}$ radicals rapidly dimerize to H_2O_2 (De et al. 1999; Legrini et al. 1993). The ($HO_2^{\bullet}$) undergo a chain termination reaction, and in aqueous solutions, H_2O_2 dissociates to form an HO_2^- anion and O_2 in a chain reaction (Metelista 1971; Venkatadri and Peters 1993). Moreover, the hydroperoxyl radicals are less reactive than the hydroxyl radicals with oxidation potentials that are much lower. Thus, the applied hydrogen peroxide concentration is important to optimize because excess can lower the treatment efficiency of AOPs (Eul et al. 1992).

Figure 3 shows the removal efficiency of cyanide and COD by the UV/H_2O_2 process under varying hydrogen peroxide concentrations at a constant pH of 10. When the hydrogen peroxide concentration was increased, inhibition was observed because of the radical scavenging effect.

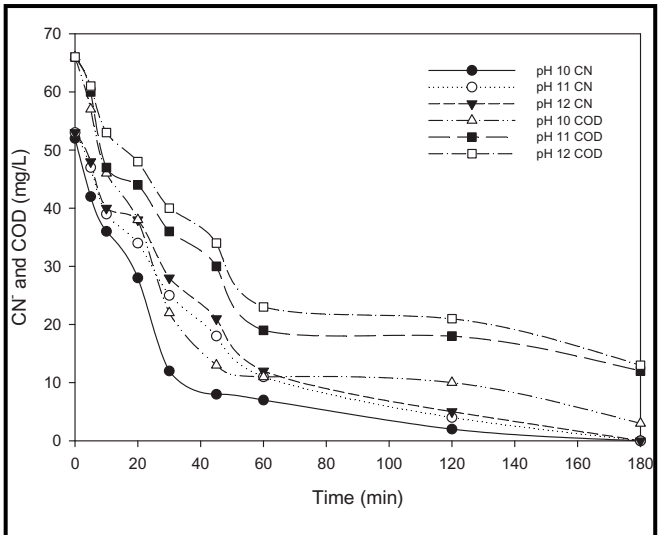

FIGURE 2. Cyanide and COD removal at different pH values (CH_2O_2 = 100 mg/L) for the UV/H_2O_2 process.

In previous studies, several research groups working on photodegradation of other organic compounds described an optimum dose of H_2O_2 (Azbar et al. 2004; De et al. 1999; Gulyas 1997; Ho 1986; Ince 1999; Ku et al. 1998; Noss and Chyrek 1984; Shu et al. 1994).

UV alone was not effective in the degradation of cyanide, COD and TOC. When UV was used alone, after irradiation of 180 min, 50 mg/L of cyanide ion, 65.23 mg/L of COD and 17.82 mg/L of TOC were degraded to 48 mg/L, 63.25 mg/L, and 17.00 mg/L, respectively. However, when the UV was combined with 100–900 mg/L, the degradation rates for total cyanide and COD were much faster (Figure 3). At 180 min, the maximum cyanide, COD and TOC removal efficiencies when 700 mg/L of H_2O_2 was added were 99%, 99% and 98%, respectively (Table 2). However, the cyanide degradation rate with the addition of 900 mg/L of H_2O_2 was slower than that of the 700 mg/L dose. The excess H_2O_2 caused less reactive hydroperoxyl radicals to be produced, slowing the oxidation process (Figure 3). Thus, the optimal H_2O_2 dose and pH for the UV/H_2O_2 process were found to be as 700 mg/L and 10, respectively.

OZONATION EXPERIMENTS

Ozone (O_3) is a strong oxidizing agent and is highly efficient in removing cyanide at high pH values (Kepa et al. 2008; Monteagudo et al. 2004). At alkaline pH values, ozonation treatment efficiency was improved since oxidation by the reactive radical dominates (Staehelin and Hoigné 1982).

Cyanide reacts with ozone directly to produce cyanate. Under excess ozone, cyanate will be converted into bicarbonate ions and nitrogen gas via the reaction detailed in Equations [6] and [7] (Selm 1959; Tyler et al. 1951; Zeevalkink et al. 1980):

$$3CN^- + O_3(aq) \rightarrow 3OCN^- \qquad [6]$$

$$2OCN^- + O_3(aq) + H_2O \rightarrow 2HCO_3^- + N_2 \qquad [7]$$

The degradation of total cyanide followed a pseudo–first-order model. The oxidation rate of total cyanide can be described by Equation [8]:

$$r_{CN}{}^- = (-dC_{CN}/dt) = kd.C_{CN}.{}^-C_{O3} + k_{\bullet OH}.C_{\bullet OH}.C_{CN}{}^- \qquad [8]$$

where kd and $k^{\bullet}OH$ are the direct rate constant of the reaction between ozone and cyanide and the rate constant of the reaction between the hydroxyl radical and cyanide present in solution, respectively. In a semibatch ozonation process, concentration of dissolved ozone increases with reaction time and it usually reaches a constant value that is much lower than that of cyanide concentration. From these reasons, kinetic reactions given above cannot be simplified in this situation as cited in literature. Therefore, for the understanding of the reactivity of the tested system, the reaction rate constants determined

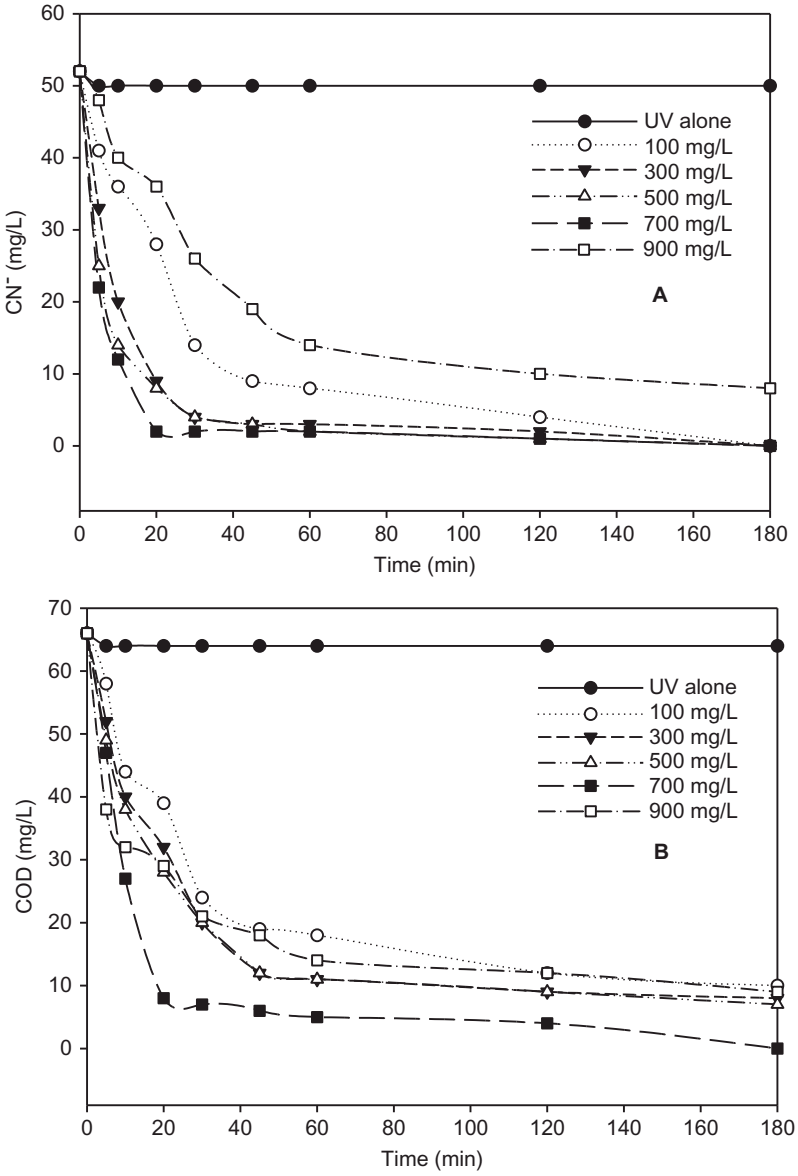

FIGURE 3. (a) Cyanide and (b) COD removal for various concentrations of H_2O_2 at a constant pH of 10 for the UV/H_2O_2 process.

absolutely empirically and these kinetic constants are only valid for this system for the determination of the reactivity of cyanide with the applied AOPs.

The presence of carbonate reduces the efficiency of AOPs because carbonate acts as a radical scavenger (Bull and Zeff 1992; Kim et al. 1997). Inhibition by carbonate influences the efficiency of most AOPs since the carbonate radicals are less reactive than the hydroxyl radicals. Lower pH values neutralizes the effect of a radical scavenger (notably ions such as carbonate and bicarbonate) leading to higher overall rates of degradation (Gogate and Pandit 2004). Ozonation treatment efficiency improved since oxidation by the reactive radical dominated. The half-life of ozone in distilled water decreases

TABLE 2. Summary of the Results of AOPs under Optimum Conditions in Terms of total Cyanide, COD and TOC Removal

AOPs	CN^- (%)	COD (%)	TOC (%)	pH	C_{H2O2} (mg/L)
UV	4	3	4	10	–
O_3	86	86	88	12	–
O_3/UV	98	96	97	10	–
H_2O_2/UV	99	99	98	10	700
O_3/H_2O_2/UV	99	99	99	10	200

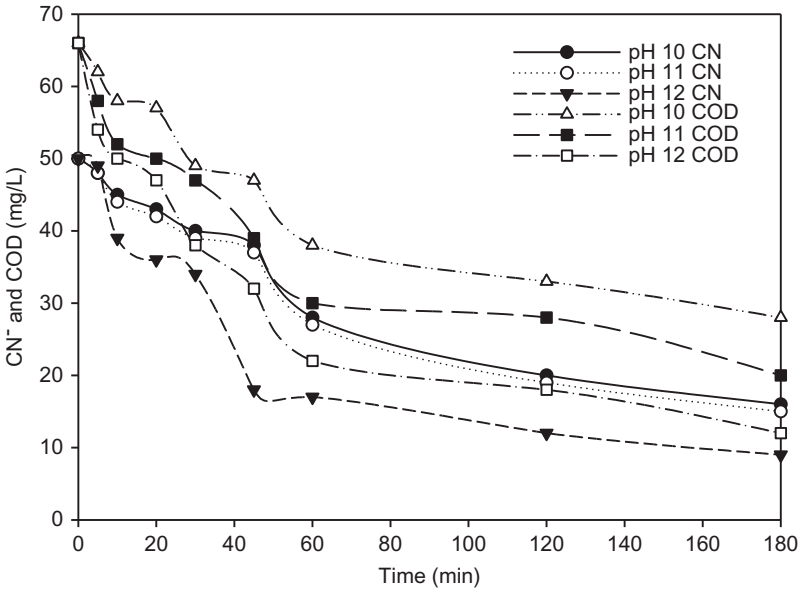

FIGURE 4. Cyanide and COD removal at different pH values for the O_3 process (C_{ozone} = 180 mg/h).

from greater than 104 s at a pH of 4 to nearly 20 s at a pH of 10 (Staehelin and Hoigné 1982).

The presence of bicarbonate, carbonate and humic substances break the closed chain reaction that started with ozone and the hydroxyl ion ($^{-}$OH) by trapping the hydroxyl radical (HO•). Additional disruptions to the reaction occur by radical-radical coupling processes and macro and/or micro pollutants in the reaction medium trapping (HO•) (Arslan 2000). Moreover, ozone reacts with other oxidizable ions such as S^{-2} to form the oxyanions $SO_3{}^{-2}$ and $SO_4{}^{-2}$ (Staehelin and Hoigné 1982). These oxidants are simple to form because the mechanism only requires the ion to come into contact with the ozone.

In this study, experiments were initially performed at varying pH values (10 < pH < 12) in order to investigate the effect of pH on CN^- and COD removal. According to Figure 4, a pH of 12 showed high CN^-, COD, and TOC removal efficiencies at room temperature (Table 2). There were no significant differences in the removal efficiencies (86% for CN^-, 86% for COD, and 88% for TOC) between the investigated pH values at the end of the 180-min reaction time. The ozone usage ratios varied in the range of 25% at a pH = 10 to 32% at a pH = 12.

O_3/UV EXPERIMENTS

The Ozone/UV process was applied to the third set of experiments in an effort to promote degradation of cyanide, COD and TOC. Prengle and Mauk (1978) was one of the first to report the beneficial effects of combining UV photolysis with the addition of ozone. Kim et al. (2003) degraded cyanide using AOPs and reported that the degradation of total cyanide in the O_3/UV process was greater than in UV/H_2O_2 (2.72 g/L). Dissolved ozone reacts in the presence of UV light to produce hydrogen peroxide (Staehelin and Hoigné 1982).

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \quad [9]$$

$$H_2O_2 + hv \rightarrow HO\bullet \quad [10]$$

$$2O_3(excess) + H_2O_2 \rightarrow 2HO\bullet + 3O_2 \quad [11]$$

This process involves the *in-situ* generation of highly potent chemical oxidants such as the hydroxyl radical (HO•) (Glaze at al. 1982; Paillard 1988).

To find the optimum pH in terms of cyanide, COD, and TOC removal, ozone on its own and in combination with both UV radiation and H_2O_2 were applied to the effluent at varying pHs. Figure 5 shows the effect of the O_3/UV process on cyanide and COD removal at different pH values. A pH of 10 showed high cyanide, COD and TOC removal efficiencies at room temperature of 98%, 96%, and 97%, respectively. The removal efficiencies were similar across all studied pH values. The combined O_3/UV process reduced the levels of cyanide, COD and TOC further than the other applied process.

O_3/UV/H_2O_2 PROCESS

To accelerate the degradation rates and demonstrate that the insertion combined process (O_3/UV/H_2O_2) is an alternative to the O_3 and O_3/UV process, the insertion combined process was applied using identical dosage of ozone.

For the O_3/UV/H_2O_2 process, the optimal pH was 10 as shown in Figure 6. Experiments were then run at pH of 10 with varying hydrogen peroxide concentrations between 25 and 300 mg/L (Figure 7). Figure 8 displays that when

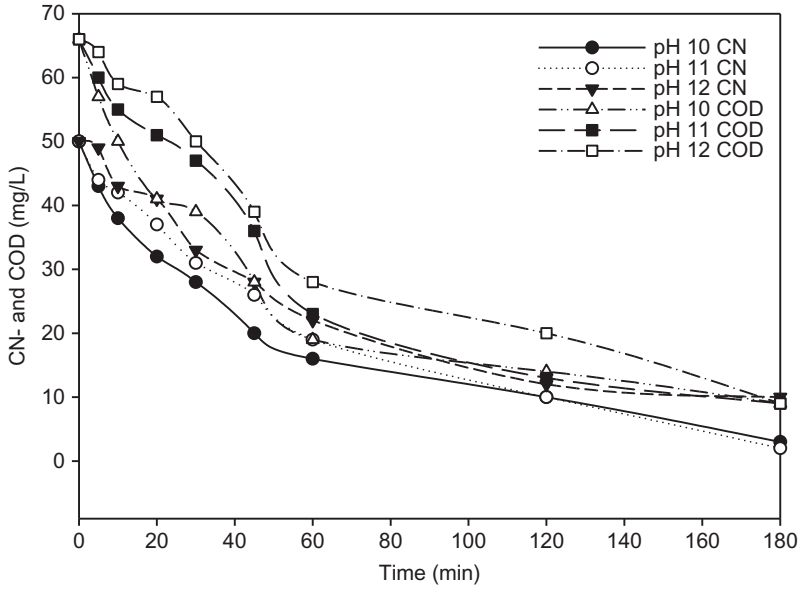

FIGURE 5. Cyanide and COD removal at different pH values for the O_3/UV process (C_{ozone} = 180 mg/h).

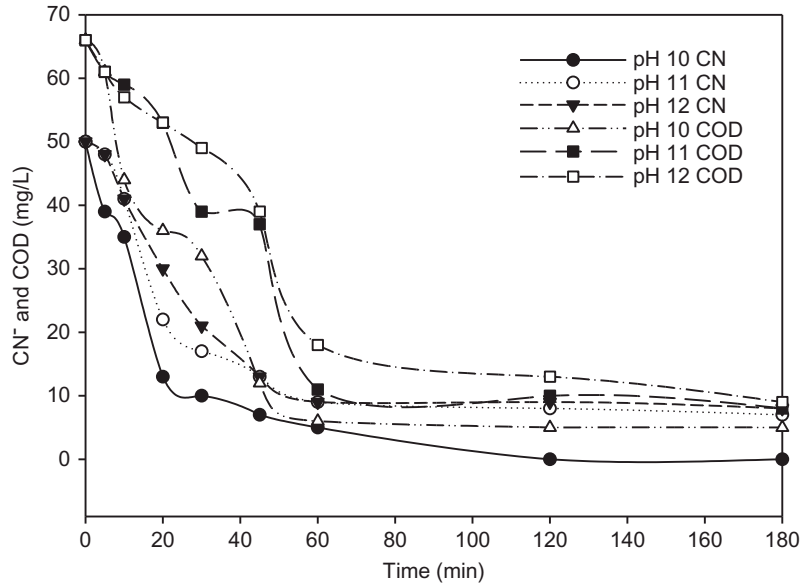

FIGURE 6. Cyanide and COD removal at different pH values (C_{H2O2} = 100 mg/L) for the O_3/UV/H_2O_2 process.

the concentration of H_2O_2 is increased, the degradation rate of cyanide increases slightly. However, the degradation rate resulting from the addition of 300 mg/L H_2O_2 was slower than the rate for the 200 mg/L dose. The optimized O_3/UV/H_2O_2 process occurred with a pH of 10 and a H_2O_2 concentration of 200 mg/L.

Table 2 displays a summary of the results for the degradation of cyanide, COD and TOC from jewelry manufacturing effluent by the different AOPs. All studied AOPs result in high CN^-, COD, and TOC removal efficiencies. O_3/UV, O_3/UV/H_2O_2 (25–300 mg/L) and UV/ H_2O_2 (100–700 mg/L) experiments resulted in removal efficiencies of 99% for CN^-, over 96% for COD and over 96% for TOC. However, the removal efficiencies of the O_3 and UV/H_2O_2 (900 mg/L) process was lower with only 86% for CN^-, over 86% for COD, and over 82% for TOC removed.

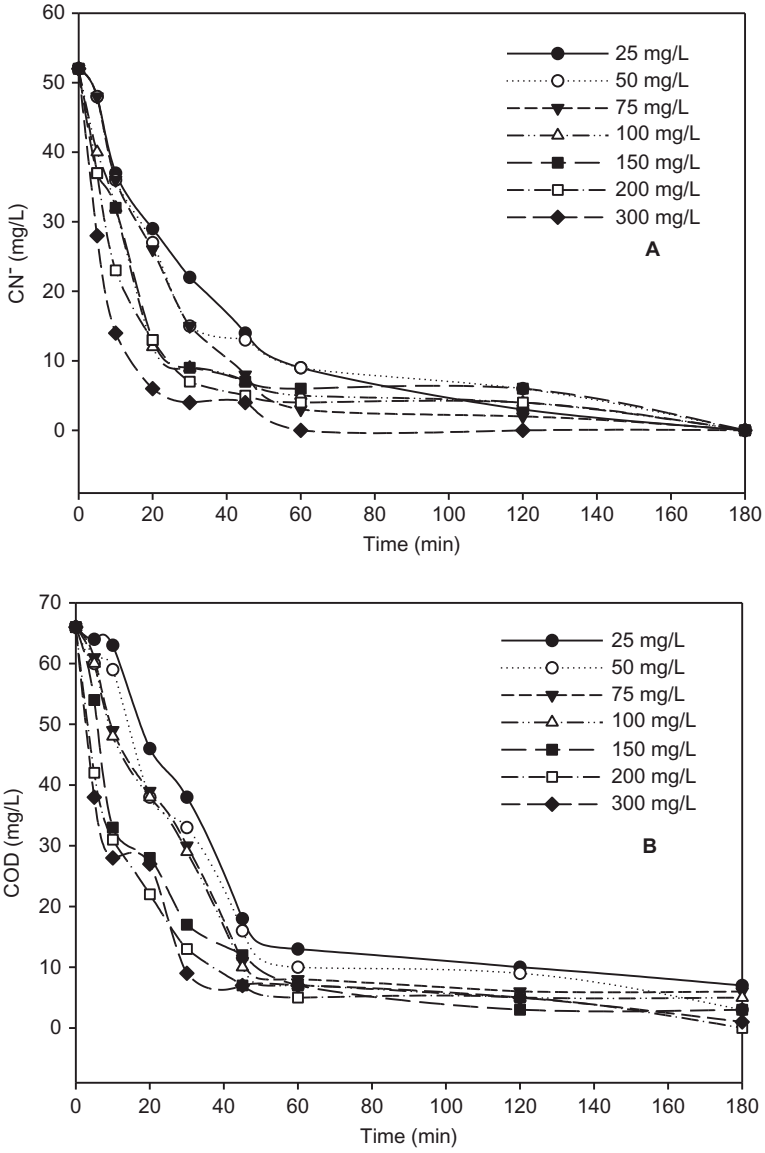

FIGURE 7. (a) Cyanide and (b) COD removal at different concentrations of H_2O_2 for the $O_3/UV/H_2O_2$ process.

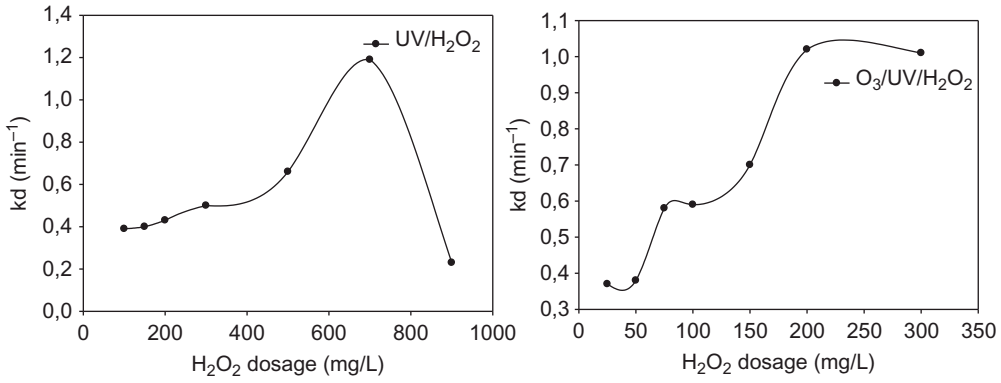

FIGURE 8. Effect of H_2O_2 dosage on pseudo–first-order kinetic coefficient for UV/H_2O_2 and $O_3/UV/H_2O_2$ processes.

CONCLUSIONS

The Advanced Oxidation Processes O_3, O_3/UV, O_3/UV/H_2O_2 and UV/ H_2O_2 were studied in this work to degrade total cyanide. The experiments were conducted at a pH range between 10 and 12 with doses of H_2O_2 between 25–900 mg/L. All of the processes studied displayed different reaction rates. In the AOPs, the degradation of total cyanide can be described by pseudo–first-order kinetics. The total cyanide degradation rate during UV/H_2O_2 (700 mg/L) treatment was the highest among all the combinations studied. 200 mg/L H_2O_2 was found to be the optimal dosage in the O_3/UV/H_2O_2 process. In the UV/H_2O_2 process, the optimal H_2O_2 dose was 700 mg/L because above this value, hydrogen peroxide acted as a radical scavenger decreasing the reaction rate. The COD removal efficiency in the O_3, O_3/UV, O_3/UV/H_2O_2 (200 mg/L), and UV/H_2O_2 (700 mg/L) process was 86%, 96%, 99%, and 99%, respectively. The TOC removal efficiency in the O_3, O_3/UV, O_3/UV/H_2O_2 (200 mg/L), and UV/H_2O_2 (700 mg/L) process was 88%, 97%, 99%, and 98%, respectively. The simple ozone treatment removed cyanide more rapidly at a pH of 12. The UV/H_2O_2 and ozonation combined with H_2O_2 and/or UV processes are faster at a pH of 10.

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