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Pre-Treatment of Antibiotic Formulation Wastewater by O_3, O_3/H_2O_2, and O_3/UV Processes

Işıl AKMEHMET BALCIOĞLU, Merih ÖTKER
Boğaziçi University, Institute of Environmental Sciences, Bebek, 34342 İstanbul-TURKEY
e-mail:balciogl@boun.edu.tr

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Abstract

The treatment of synthetically prepared antibiotic formulation wastewater with O_3, O_3/H_2O_2, and O_3/UV processes was examined. The efficiencies of the treatment processes were compared by means of COD, absorbance removals, and biodegradability enhancement. The efficiencies of O_3/pH = 7, O_3/ pH = 12, and O_3/H_2O_2(50 mM) processes were almost identical in terms of COD and UV_{254} removals. The BOD_5/COD ratio of formulation wastewater increased from 0.02 to 0.38 and 0.5 at the end of 1 hr of ozone treatment at pH = 7 and pH = 12, respectively. For the formulation wastewater subjected to O_3/UV process at pH = 7, parallel to the UV_{254} removal efficiency, a 20% increase was obtained in the Oxygen Uptake Rate (OUR) value compared to that of mere ozonation.

Key words: Antibiotic, Advanced oxidation, Formulation wastewater, Ozonation, Pharmaceutical industry wastewater.

Introduction

Among all the pharmaceutical drugs that cause contamination problems in the environment, antibiotics occupy an important place due to their high consumption rates in both veterinary and human medicine (Kümmerer, 2001). Antibiotics generally have low biodegradability since they are biocidal substances and the degradation of these substances cannot be accomplished in the natural environment or biological treatment plants (Richardson and Bowron, 1985; Kümmerer, 2001). Consequently, the antibiotics in surface and ground water were detected in the concentration range of μg/l and ng/l, respectively (Halling-Sorensen *et al.*, 1998). Toxic effects of low concentrations of antibiotics on aquatic organisms have been investigated in the mg/l range (Kümmerer *et al.*, 2000; Wollenberger *et al.*, 2000).

Despite the presence and chronic toxic effects of antibiotics in the aquatic environment, few studies reported in the literature have dealt with the treatment of these substances (Adams *et al.*, 2002; Balcıoğlu and Ötker, 2002; Balcıoğlu and Ötker, 2003). It was found that conventional biological treatment systems were not effective in the removal of antibiotics (Kümmerer *et al.*, 1997; Ingerslev and Halling-Sorensen, 2000); therefore, it is clear that chemical oxidation technologies are necessary for the removal of this kind of pollutant.

In view of the above-mentioned facts, antibiotic formulation wastewater containing enrofloxacin was subjected to O_3, O_3/H_2O_2 and O_3/UV processes in order to enhance its biodegradation.

Materials and Methods

Synthetic formulation wastewater

The synthetic antibiotic formulation wastewater was prepared by dissolving specific amounts of formulation mixture containing 10% enrofloxacin active substance in distilled water. The absorption spectrum of synthetic formulation wastewater is presented in Figure 1, together with the molecular structure of enrofloxacin, a quinolone group antibiotic.

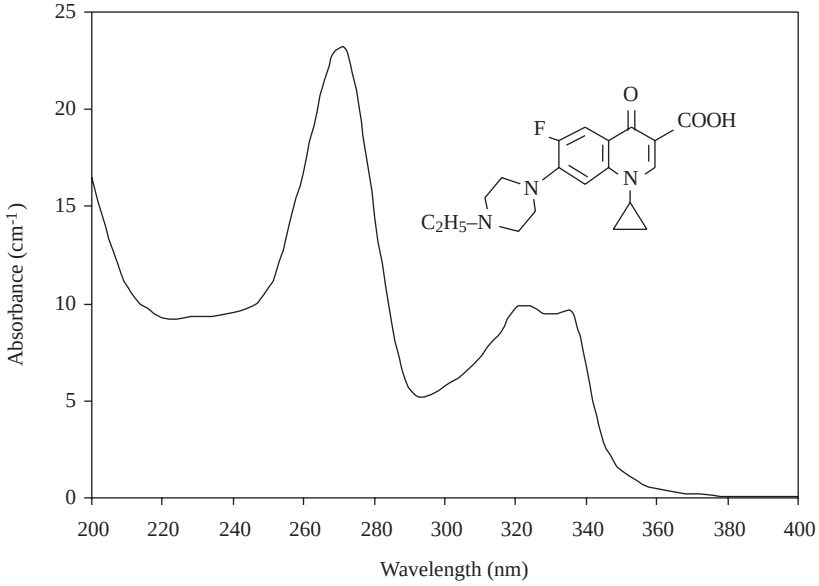

Figure 1. Absorption spectra of the formulation wastewater (COD_i = 450 mg/l) and the molecular structure of enrofloxacin.

As can be seen from Figure 1, enrofloxacin formulation wastewater exhibited the maximum absorption at 272 nm and 334.5 nm wavelengths.

Ozone reactor

O_3 and O_3/H_2O_2 processes were performed in a 1.5 l capacity borosilicate glass ozone bubble column, while the O_3/UV process was conducted in a 2 l photoreactor in semi–batch mode with respect to ozone supply. Ozone was produced from dry, pure oxygen in a laboratory scale ozone generator unit (Fisher OZ 500). The applied ozone concentration ranged between 960 mg/h and 4440 mg/h. The O_2+O_3 gas mixture was delivered from the bottom of reactors through sintered glass discs at a rate of 100 l/h. Ozone mass transfer coefficients (K_La) of the ozone bubble column and photoreactor were determined as 1.78 and 0.62 min^{-1}, respectively (Ötker, 2002). The photoreactor was equipped with a 20 W low pressure mercury lamp that emitted mainly at λ = 254 nm, and the lamp was placed into a quartz envelope. The incident photonic flux of the photochemical reactor was determined by H_2O_2 actinometry as 4.5 W/l.

Analytic measurements

The spectrophotometric measurements were performed by a Shimadzu UV-1208 model spectrophotometer at 272 nm, 334.5 nm, and 254 nm wavelengths. Parent compound degradation was traced in terms of absorbance reduction at 272 nm and 334.5 nm wavelengths. UV_{254} represents the aromatic content of wastewater (Ravikumar and Gurol, 1994). The Oxygen Uptake Rate (OUR) of the ozonated samples was determined by a WTW Oxi 3000 model respirometer equipped with a microprocessor. BOD_5 and COD measurements were conducted in accordance with Standard Methods (APHA/AWWA/WPCF, 1989). Ozone concentrations in the feed and off – gas were measured iodometrically at regular time intervals.

Results and Discussion

Application of O_3 and O_3/H_2O_2 processes to the formulation wastewater

Since pharmaceutical industry formulation wastewater is generated from the cleaning operations of formulation equipment, the composition of wastewater consists solely of the formulation mixture. The concentration of pollutants present in the wastewater depends upon the amount of water used for the cleaning operation. Our studies carried out on actual veterinary antibiotic formulation wastewater indicated that the COD values ranged from 300 to 1000 mg/l.

Preliminary experiments indicated that during the 1 h ozonation process the pH of the antibiotic formulation wastewater decreased significantly (from pH = 7 to pH = 2.8) due to the formation of acidic reaction products. As the ozonation treatment time

progressed, the COD removal rate of the synthetic wastewater also slowed down. This result can be explained by the fact that the oxidation mechanism in the ozonation process is pH dependent. Therefore, experiments were conducted using phosphate buffer solutions in order to eliminate the changes in pH during the ozonation treatment. The overall COD removal rate of wastewater (COD_i = 450 mg/l) obtained in the 1 h ozonation treatment period at pH = 7 was 16% lower that achieved by the ozonation process performed in the presence of the phosphate buffer (Ötker, 2002).

It is well known that hydrogen peroxide (H_2O_2) can be used in combination with ozone in order to increase the oxidation efficiency of refractory compounds (Staehelin and Hoigne, 1982). In this study, the effect of H_2O_2 on the ozonation process for the treatment of formulation effluent (COD_i = 450 mg/l) was studied at 5 different concentrations of H_2O_2 (10–75 mM) at pH = 7. The addition of H_2O_2 up to 50 mM only slightly improved the overall COD values. However, a further increase in the introduced H_2O_2 dose resulted in a significant reduction in the overall COD abatement, since H_2O_2 at high concentrations acts as a radical (Glaze *et al.*, 1987). Figure 2 displays the normalized COD and UV_{254} values of the synthetic formulation effluent treated by mere ozonation at pH = 3, 7, and 12, and in the presence of 50 mM H_2O_2 at pH = 7 as a function of treatment time.

The results presented in Figure 2 indicate that by increasing the ozonation pH from 3 to 12, overall COD and UV_{254} removals improved from 65% to 87% and from 82% to 99%, respectively. Although the ozone absorption was increased by the increment of the wastewater pH from 7 to 12 (data not shown), COD and UV absorbance removals remained almost constant. Even if a rapid decrease in the COD and UV_{254} values was observed within the initial period of the ozonation process at pH = 3, the progress of the treatment time resulted in a lower treatment efficiency due to the formation of reaction products that are resistant to oxidation by molecular ozone. On the other hand, at alkaline pH values, ozonation treatment efficiency was improved since the reactive radical oxidation dominated. In addition, absorbance values at the wavelengths of 272 and 334.5 nm, which characterized the functional groups of enrofloxacin, decreased rapidly and their complete removal was achieved at the end of the 1 h ozonation period at 3 different pH values. Complete removal of the active substance was also confirmed by the HPLC analysis (Balcıoğlu and Ötker, 2002)

In another study performed in our laboratory, the addition of H_2O_2 at the optimum dosage to the ozonation process significantly enhanced the treatment efficiency of the penicillin formulation effluent (Balcıoğlu and Ötker, 2003). However, in this study, COD and UV_{254} abatements obtained by the O_3/H_2O_2 process were found to be almost identical with the results of the ozonation process performed at pH 7 and 12.

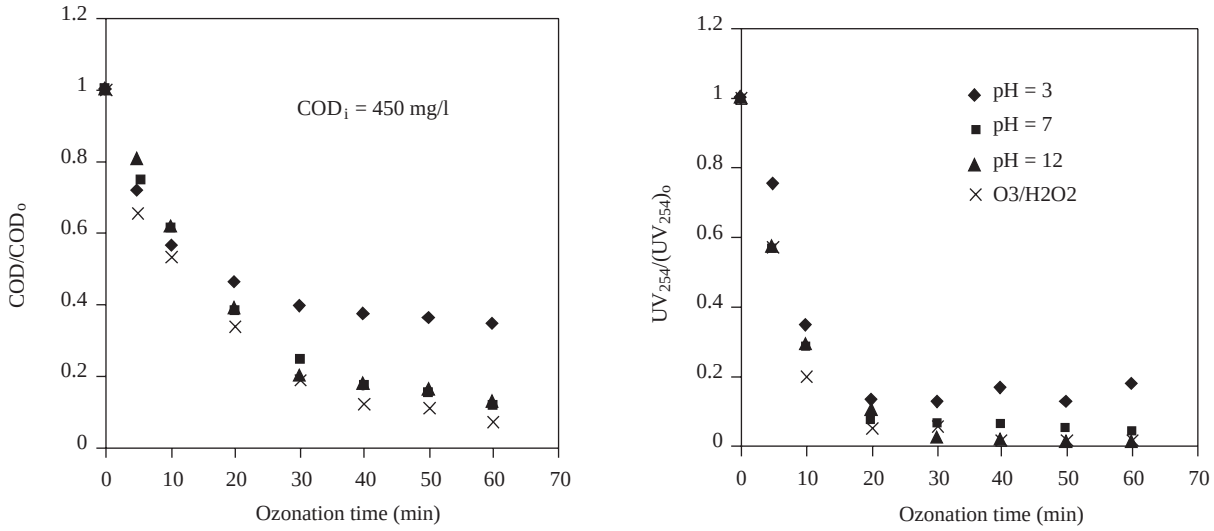

Figure 2. Changes in the COD and UV_{254} values by the application of O_3 and O_3/H_2O_2 processes (applied ozone dose = 2960 mg/l.h).

Due to the fluctuation in wastewater quality, it is of practical interest to examine how the COD value of wastewater affects the efficiency of the ozonation process. Experiments were carried out at 3 different initial COD values of synthetic wastewater with an applied ozone dose of 2960 mg/l.h and the results obtained are presented in Figure 3 in terms of the normalized COD and UV_{254} as a function of ozonation time.

With the lower initial COD value of the synthetic formulation effluent, higher treatment efficiency in terms of COD and UV_{254} abatement was achieved. In spite of the decrease in the efficiency of ozonation, the overall COD and UV_{254} removals of the formulation wastewater with the highest initial COD value (COD_i = 900 mg/l) were still high (Figure 3).

At 4 different dosages (640 mg/l.h–2960 mg/l.h), ozone was applied to the synthetic antibiotic formulation effluent having an initial COD value of 900 mg/l at pH = 7 in order to elucidate the effect of ozone dose on the treatment efficiency. The results obtained are presented in Figure 4 in terms of the overall COD and UV_{254} removal and the BOD_5/COD ratio together with the variations in the amount of absorbed ozone. The difference between the inlet and outlet ozone gas concentration was determined as absorbed ozone by the enrofloxacin containing formulation wastewater.

As the applied ozone dose was increased from 640 mg/l.h to 2592 mg/l.h, a 3-fold improvement in the BOD_5/COD ratio was established. A further increase in the applied ozone concentration did not cause an important change in the biodegradability of the wastewater or the amount of absorbed ozone under the conditions used in this study.

It has been shown that the biodegradability of industrial wastewater can be improved with ozonation, and the BOD_5/COD ratio can be increased from 0 to 0.15 and 0.5 under optimum conditions (Scott and Ollis, 1995; Alvares, 2001). In this study, by the application of 2592 mg/l.h of ozone, the BOD_5/COD ratio of antibiotic formulation wastewater was increased from 0.02 to 0.35 at pH = 7. In addition, at pH = 12, with an applied ozone dose of 2960 mg/l.h, the BOD_5/COD ratio was raised to 0.5. The results of this study and others reported in the literature illustrate the need to determine the optimum ozone dose to achieve the desirable biodegradability for industrial wastewaters.

In the pharmaceutical industry, the production of different drugs in a short time interval causes variations in the pollutant load and in the composition of wastewater. The aim of pretreatment is to achieve the highest biodegradability of wastewater. In order to evaluate the effect of ozonation time on the biodegradability of the formulation wastewater (COD_i = 900 mg/l), BOD_5 and OUR values of 15, 30, 45, and 60 min ozonated samples were determined (Figure 5).

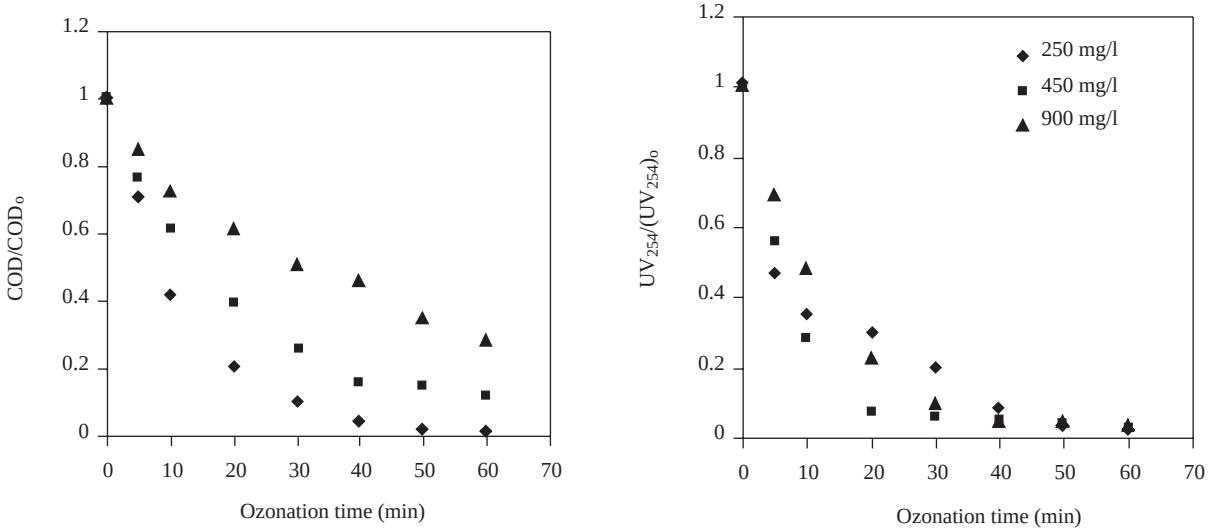

Figure 3. Effect of the initial COD value of the formulation wastewater on ozonation efficiency.

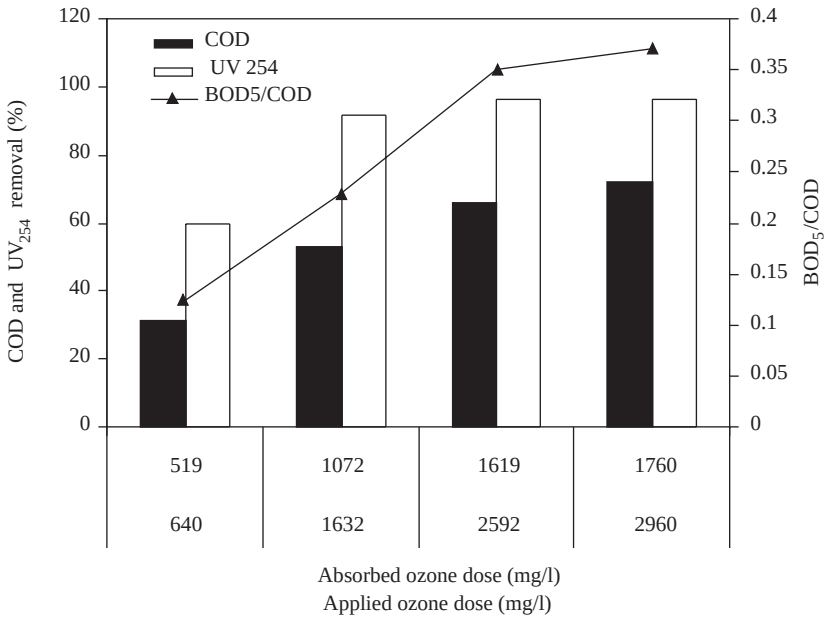

Figure 4. Effect of the applied ozone dose on COD and UV_{254} removal and the BOD_5/COD ratio.

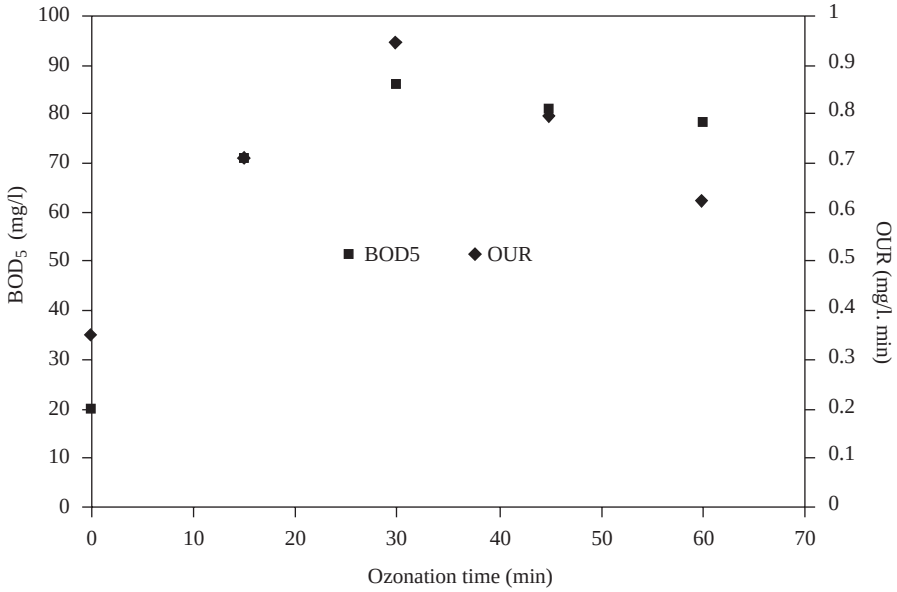

Figure 5. Changes in BOD_5 and OURs of the antibiotic formulation wastewater by the application of ozone (applied ozone dose = 2960 mg/l.h).

OUR and BOD_5 of the synthetic wastewater reached maximum values within the first 30 min of the ozonation process. However, a further increase in the ozonation time period caused lower biodegradability of the wastewater.

Application of the O_3/UV process to formulation wastewater

Photolytic ozonation has been shown by several investigators to be more effective in the destruction of some organic compounds found in wastewater than ozonation alone. Especially in cases where an organic substance has a strong absorption in the UV

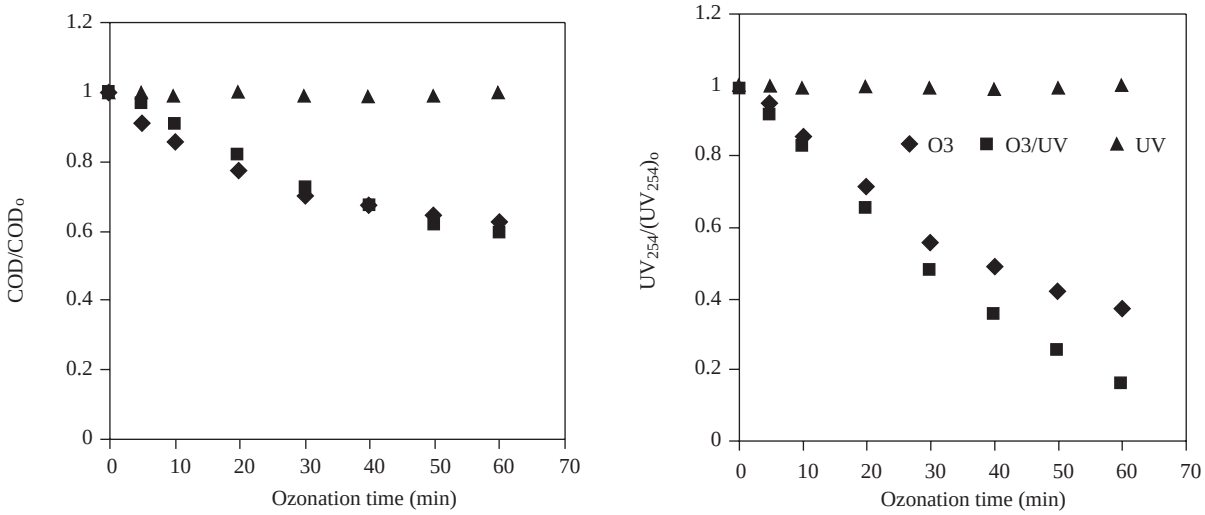

Figure 6. Comparison of O_3, O_3/UV and UV processes in terms of COD and UV_{254} abatement (applied ozone dose = 2220 mg/l.h).

region of the spectrum, large fluxes of UV irradiation accelerate the destruction of the substance (Peyton *et al.*, 1982; Ku *et al.*, 2000; İkiz, 2003). In order to examine the contribution of UV radiation to the efficiency of the ozonation process, synthetic formulation wastewater was subjected to an O_3/UV process at pH 7. Figure 6 illustrates the comparison of the O_3, O_3/UV and UV processes in terms of COD and UV_{254} abatements.

Although the combination of UV light and ozone did not make a significant contribution to the overall COD removal, it provided 20% and 24% increases in aromaticity removal and the amount of absorbed ozone, respectively. Parallel to the increase in aromaticity removal, OUR values for the 30 and 60 min ozonated formulation wastewaters were also improved by about 20% by means of the photolytic ozonation process.

Conclusion

The results of this study indicate that for the treatment of antibiotic formulation wastewater by ozonation, pH control is an important factor in order to obtain an effective treatment performance. By means of the application of ozonation at pH = 12, the BOD_5/COD ratio could be improved to 0.5. The introduction of H_2O_2 did not enhance the treatment efficiency of the enrofloxacin containing formulation wastewater. In the O_3/UV process, the contribution of UV light to the overall aromaticity removal and biodegradability enhancement was high. Consequently, ozonation and photolytic ozonation processes seem to be promising methods for the pretreatment of antibiotic containing formulation wastewaters.

Acknowledgments

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