

Effects of Adding UV and H₂O₂ on the Degradation of Pharmaceuticals and Personal Care Products during O₃ Treatment

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Abstract

The degradation of 30 pharmaceuticals and personal care products (PPCPs) subjected to O₃, O₃/UV, and O₃/H₂O₂ treatments were investigated using semi-batch tests and evaluated by their pseudo-first-order rate constants. The additional application of UV or H₂O₂ during O₃ treatment significantly improved the degradation rate of most of the PPCPs. At the same O₃ feed rate, O₃/UV treatment exhibited much higher PPCP degradation efficiency than that of O₃ treatment. This was probably due to degradation of the PPCPs by O₃, direct UV photodegradation, and OH radicals that formed from the photodegradation of O₃ during O₃/UV treatment. PPCP degradation by O₃ was also promoted by adding H₂O₂ during the O₃ treatment. However, when the initial H₂O₂ concentration was high during O₃ treatment, OH radicals were likely to be scavenged by excess H₂O₂, leading to low PPCP degradation. Therefore, it is important to determine the appropriate H₂O₂ dosage during O₃ treatment to improve PPCP degradation when adding H₂O₂ during O₃ treatment.

Keywords: O₃, O₃/H₂O₂, O₃/UV, Pharmaceuticals, PPCPs

1. Introduction

The main reasons for the use of O₃ are disinfection and oxidation such as taste and odor control, decolorization, and elimination of micropollutants. Similar to other disinfectants such as chlorine or chlorine dioxide for water treatment, O₃ is unstable in water, and undergoes reactions with some water matrix components. However, O₃ decomposes, generating OH radicals, which are strong oxidants in water [1]. The disinfection process occurs mainly through the reaction of O₃ molecules, whereas the oxidation process may occur through both O₃ and OH radicals [2]. O₃ reacts with a variety of inorganic and organic compounds. However, the fact that rate constants for the O₃ reaction range over several orders of magnitude means that O₃ is a very selective oxidant. O₃ reacts quickly with phenols, amines, compounds with C = C double bonds, and aromatic compounds.

O₃-based advanced oxidation processes (AOPs) are applied to oxidize O₃-resistant compounds such as pesticides and chlorinated solvents by OH radicals, which are powerful and non-selective oxidants. OH radicals react very quickly with various inorganic and organic compounds in water. Therefore, OH

radicals also contribute to the oxidation of micropollutants. However, their efficiency is often limited by the scavenging effect of the water matrix. In O₃-based AOPs, the formation of OH radicals is accelerated by increasing the pH of the water, by dosing H₂O₂, or by adding UV irradiation. This ensures faster oxidation of O₃-resistant compounds.

Potential risks associated with the release of pharmaceuticals and personal care products (PPCPs) into the aquatic environment have become an increasingly important issue for environmental regulators and the pharmaceuticals industry [3]. Therefore, the use of appropriate PPCP removal technologies should be applied in wastewater treatment plants to limit the aquatic risk of PPCPs. Many studies have been conducted on the degradation of PPCPs by O₃-based processes, showing that O₃ was the oxidant, although some PPCPs seem to be resistant to O₃ [4-7]. A great variety of PPCPs are being used in daily life and have been detected in the water environment [3, 8, 9]. Nevertheless, a limited number of PPCPs have been investigated because of the difficulty of the PPCPs analysis. The objective of this study was to investigate the effects of H₂O₂ and UV on the degradation of 30 PPCPs during O₃ treatment.

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2. Materials and Methods

2.1. Selected PPCPs and Preparation of Test Water

The 30 PPCPs selected in this study consisted of analgesics, antiarrhythmic agents, antibiotics, bronchodilators, an anti-itching drug, anticonvulsants, antineoplastic agents, insect repellents, a carbadox (antiparasitic agent) intermediate, and an *N*-methyl d-aspartate receptor antagonist. Detailed information on the 30 PPCPs and their analytical method using high performance liquid chromatography-mass spectroscopy/mass spectroscopy (HPLC-MS/MS) was provided in our previous study [10]. To examine the degradability of the 30 PPCPs using O₃, O₃/UV, and O₃/H₂O₂, test water samples were prepared by spiking the 30 PPCPs into pure water obtained from Nisso Shoji Co., Ltd (Tokyo, Japan). The initial concentrations of the 30 PPCPs in the

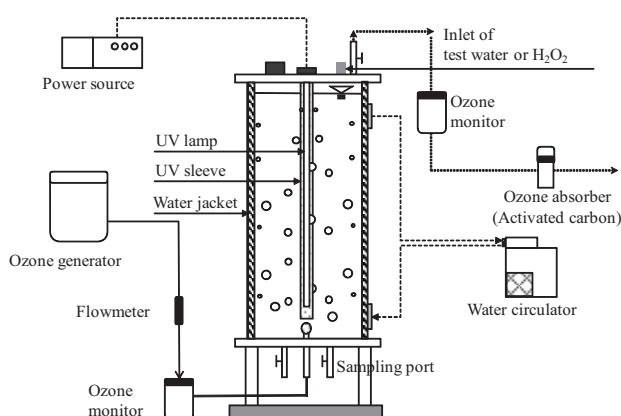


Fig. 1. Semi-batch reactor for the O₃, O₃/UV, and O₃/H₂O₂ treatment experiments.

Table 1. Measurement conditions of the high performance liquid chromatography-mass spectroscopy/mass spectroscopy (HPLC-MS/MS) for the pharmaceuticals and personal care products (PPCPs) analysis

<HPLC : Waters 2659>				
- Column: Waters SunFire C18 2.1 mm × 150 mm, 5 μm				
- Column Temp.: 20°C				
- Flow rate: 0.2 mL/min				
- Injection volume: 10 μL				
- Mobile Phase: A Water, B Methanol, C 1% Formic acid				
Gradient Time(min)	A(%)	B(%)	C(%)	
0	70	20	10	
15	0	90	10	
20	70	20	10	
<MS/MS : Quattro micro API>				
- Ionization: Electrospray Ionization(ESI) Positive				
- Spray Voltage: 3.5 kV				
- Capillary Temp.: 350°C - Source Temp.: 120				

test water samples ranged from 4.7 μg/L (mefenamic acid) to 147.6 μg/L (sulfamonomethoxine). The procedure for the preparation of the test water is described elsewhere [10].

2.2. Analytical Method

The 30 PPCPs were quantified simultaneously with a HPLC/MS/MS. An HPLC Alliance Waters2695 separation module (Water Inc., Milford, MA, USA) and a Quattro micro API tandem mass spectrometer were used for the HPLC and the MS/MS, respectively. MassLynx™ Software (Waters) managed the control of the HPLC/MS/MS system and treatment of the data acquired during the operation of HPLC/MS/MS. A gradient elution analysis method by varying mobile phase polarity with time was adopted to simultaneously quantify the 30 PPCPs. Samples taken during the experiments were introduced directly to HPLC/MS/MS. Table 1 shows the measurement conditions for HPLC/MS/MS in detail.

2.3. Experimental Setup and Conditions

All of the experiments were conducted using a cylindrical stainless reactor (Fig. 1). The temperature of the test water samples was maintained at 20°C with a hot water circulator. The pH of all test water samples, prepared by spiking the 30 PPCPs into pure water (PW), was adjusted to 7.0 with a 1 M phosphate buffer solution. Treatment experiments started by continuously injecting O₃ gas into the reactor. We conducted three different treatment experiments (O₃, O₃/UV, and O₃/H₂O₂) to compare the degradation characteristics of each PPCP.

An O₃ treatment experiment was performed under three different O₃ feed rates of 0.15, 0.3, and 0.6 mg/L/min. In this study, O₃ feed rate was controlled by supplying O₃ gas to the reactor at concentrations of 3.3, 6.6, and 13.2 mg/L, respectively, and by maintaining the flow rate of O₃ gas at a constant 1.0 L/min during all experiments.

An 8 W low-pressure mercury lamp emitting radiation at 254 nm with a UV intensity of 0.384 mW/cm² was used for O₃/UV treatment. The O₃/UV treatment was performed on test water prepared with PW at O₃ feed rates of 0.15, 0.3, and 0.6 mg/L/min. The O₃/H₂O₂ treatment was performed by adding H₂O₂ solution to the test water before O₃ treatment. Initial H₂O₂ concentrations of 2.3 mg/L and 11.2 mg/L in the test water prepared with PW were used, and the O₃ feed rate was 0.6 mg/L/min in both experiments.

3. Results and Discussion

3.1. Determination of the PPCP Rate Constants for the O₃, O₃/UV, and O₃/H₂O₂ Treatments

The degradation reaction of an organic compound by O₃ is generally expressed as [11]:

$$-\frac{d[C]}{dt} = k[O_3][C] = k'_{O_3}[C] \quad (1)$$

where [C] is the concentration of the organic compound, *k* is the first order rate constant, [O₃] is the concentration of dissolved O₃, and *k'*_{O₃} is the pseudo first-order rate constant. Pseudo first-order conditions are met if [O₃] ≥ 10 × [C], and [O₃] does not

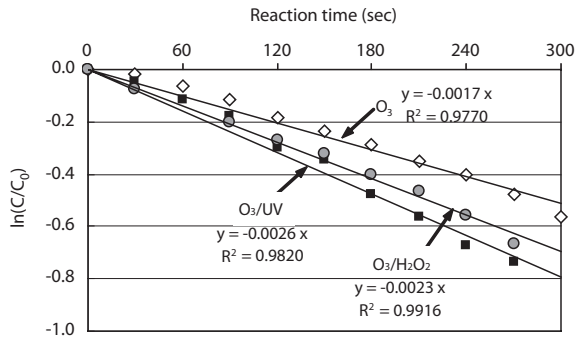


Fig. 2. Decrease in concentration of *N,N*-diethyl-*m*-toluamide (DEET) with time during O₃, O₃/UV, and O₃/H₂O₂ treatments (O₃ feed rate: 0.6 mg/L/min, UV intensity: 0.384 mW/cm², initial H₂O₂ concentration: 11.2 mg/L).

self-decay significantly during the reaction [12]. For experiments using the same reactor, the k'_{O_3} value can be used as an indicator for the reactivity of an organic compound with O₃. Integrating Eq. (1), we obtain

$$\ln(C_t / C_0) = k'_{O_3} t \quad (2)$$

where C_t is the concentration of the organic compound at the reaction time t , and C_0 is the initial concentration of the organic compound.

In the case of O₃/UV treatment, the organic compound is degraded by O₃, direct UV photodegradation, and OH radicals formed by UV photodegradation of O₃. Therefore, the decrease in concentration of the organic compound during O₃/UV treatment can be expressed as:

$$-\frac{d[C]}{dt} = (k[O_3] + 2.3LI_0\phi\epsilon + k_r[OH\cdot])[C] \quad (3)$$

Integrating Eq. (3), we obtain

$$\ln(C_t / C_0) = (k[O_3] + 2.3LI_0\phi\epsilon + k_r[OH\cdot])t = k'_{O_3/UV}t \quad (4)$$

where L is the reactor optical light path (cm), I_0 is the UV intensity (einstein/sec), ϕ is the quantum yield (mol/photon), ϵ is the molar extinction coefficient of the organic compound (l/M/cm), k_r is the second-order rate constant of OH radicals, and $[OH\cdot]$ is the concentration of OH radicals.

In the case of O₃/H₂O₂ treatment, the organic compound is mainly degraded by O₃ and OH radicals, so the decrease in concentration of the organic compound can be expressed as follows:

$$-\frac{d[C]}{dt} = (k[O_3] + k_r[OH\cdot])[C] \quad (5)$$

Integrating Eq. (5), the following expression is obtained:

$$\ln(C_t / C_0) = (k[O_3] + k_r[OH\cdot])t = k'_{O_3/H_2O_2}t \quad (6)$$

If the $\ln(C_t/C_0)$ of an organic compound decreases linearly with time, the degradation reaction of the compound by each treatment can be regarded as a pseudo-first-order reaction. In this case, the pseudo-first-order rate constants (k'_{O_3} , $k'_{O_3/UV}$, and

k'_{O_3/H_2O_2}) for O₃, O₃/UV, and O₃/H₂O₂, respectively, are obtained from the slopes of each straight line.

Fig. 2 shows the decrease in concentration of *N,N*-diethyl-*m*-toluamide (DEET) for a reaction time of 5 min during the O₃, O₃/UV, and O₃/H₂O₂ treatments, which were conducted using test water samples prepared by simultaneously spiking the 30 PPCPs into pure water. O₃ was supplied to the reactor at a feed rate of 0.6 mg/L/min in all experiments. O₃/H₂O₂ treatment was performed by supplying O₃ to the test water samples with an initial H₂O₂ concentration of 11.2 mg/L. Regardless of the treatment method, the DEET concentration decreased linearly with time. Therefore, the degradation reactions of DEET with O₃, O₃/UV, and O₃/H₂O₂ conformed with pseudo-first-order reactions under the experimental conditions of this study. As shown in Fig. 2, the value of k'_{O_3} (the pseudo-first-order rate constant for O₃) of DEET was 1.7×10^{-3} /sec, whereas that of k'_{O_3/H_2O_2} was slightly enhanced at 2.3×10^{-3} /sec due to the contribution of OH radicals to DEET degradation. Moreover, the value of $k'_{O_3/UV}$ increased by 2.6×10^{-3} /sec as a result of adding UV to the O₃ treatment.

A linear decrease in concentration for a 5 min reaction time was shown by all of the PPCPs selected in this study, irrespective of the applied treatment methods, and the pseudo-first-order rate constants of the 30 PPCPs for each process could be obtained from the slope of each straight line. The pseudo-first-order rate constants were used to compare the degradability of the 30 PPCPs using each treatment method as well as the effects of adding H₂O₂ and UV during O₃ treatment on PPCP degradation.

3.2. Effect of UV on PPCP Degradation during O₃ Treatment

Fig. 3 compares the pseudo first-order rate constants of the 30 PPCPs for O₃ treatment with/without UV under O₃ feed rates of 0.15, 0.3, and 0.6 mg/L/min, respectively. The combination of UV during O₃ treatment led to a distinct improvement in degradation rates of most of the PPCPs. Rate constants of several PPCPs such as ketoprofen, diclofenac, sulfamethoxazole, and antipyrine increased considerably by adding UV during the O₃ treatment. In particular, ketoprofen and diclofenac showed much higher rate constants than those for O₃ treatment, regardless of the O₃ feed rate. Our previous study showed that ketoprofen and diclofenac are degraded very easily with UV, indicating that direct UV photodegradation mainly contributes to its degradation during UV/H₂O₂ treatment [11]. In this study, it was thought that such fast degradation of ketoprofen and diclofenac could be attributed to direct UV photodegradation rather than to OH radicals during O₃/UV treatment.

The degradation efficiencies of the 30 PPCPs with each treatment were compared to investigate the effect of O₃ feed rate on PPCP degradation during the O₃ and O₃/UV treatments. The degradation efficiency was calculated as the ratio of the average rate constant (l/sec) for all PPCPs to the O₃ consumption per volume of reactor (mg/L). As a result, 1.6×10^{-3} , 2.2×10^{-3} , and 1.8×10^{-3} l/mg/sec were obtained for O₃ feed rates of 0.15, 0.3, and 0.6 mg/L/min, respectively, during O₃ treatment. The degradation efficiencies following O₃/UV treatment were 6.9×10^{-3} , 3.8×10^{-3} , and 3.3×10^{-3} l/mg/sec for O₃ feed rates of 0.15, 0.3, and 0.6 mg/L/min, respectively, showing apparently increased values compared to those for O₃ treatment. However, in contrast to the O₃ treatment, the highest degradation efficiency was observed at a low O₃ feed rate of 0.15 mg/L/min, indicating that the O₃ dose required for PPCP degradation can be reduced by combining UV and O₃ treatment.

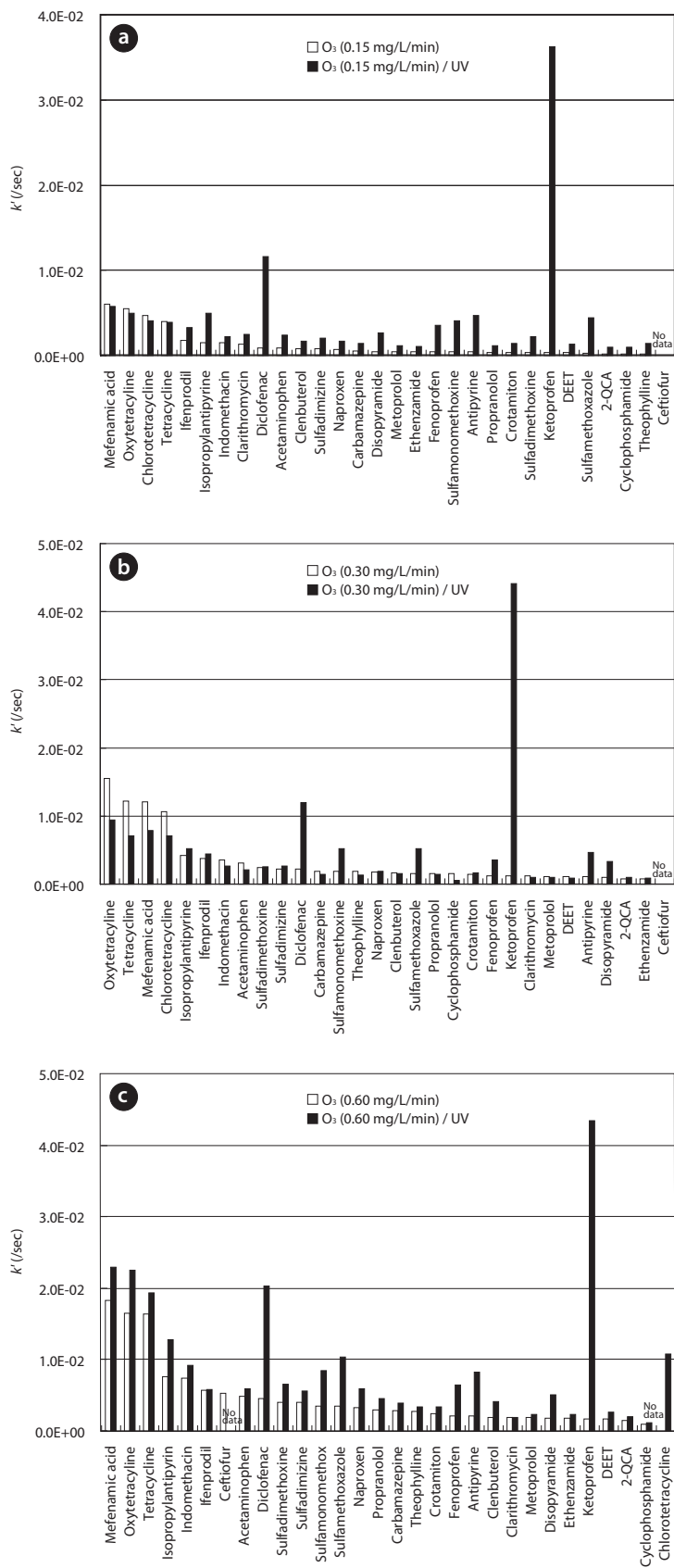


Fig. 3. Comparison of rate constants of the 30 pharmaceuticals and personal care products (PPCPs) during O₃ treatment with/without UV. (a) O₃ feed rate, 0.15 mg/L/min, (b) O₃ feed rate, 0.3 mg/L/min, and (c) O₃ feed rate, 0.6 mg/L/min.

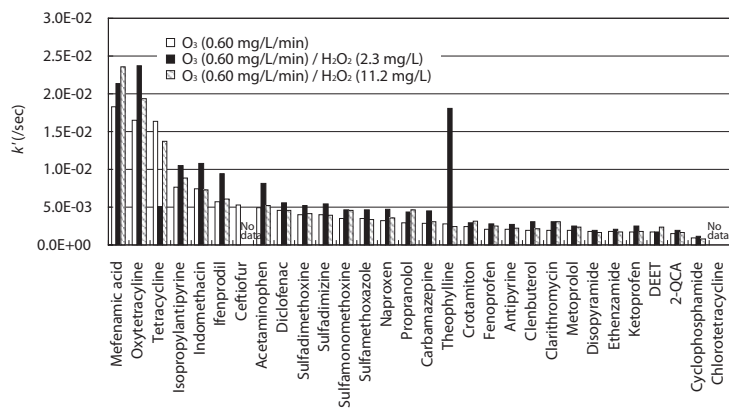
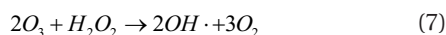


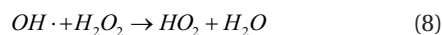
Fig. 4. Comparison of rate constants of the 30 pharmaceuticals and personal care products (PPCPs) during O₃ treatment with/without adding H₂O₂.

3.3. Effect of Adding H₂O₂ on PPCP Degradation during O₃ Treatment

Fig. 4 compares the rate constants of the 30 PPCPs after O₃/H₂O₂ treatment with the k' values obtained for O₃ treatment using an O₃ feed rate of 0.6 mg/L/min. O₃/H₂O₂ experiments were conducted by maintaining the initial H₂O₂ concentrations in tested water at 2.3 mg/L and 11.2 mg/L before injecting O₃ gas into the tested water. No variation was observed in the PPCP concentrations when only H₂O₂ was added to the PPCP-tested water. Here, the rate constants of 28 PPCPs were discussed, except ceftiofur and chlorotetracycline, for which peaks were not observed. O₃ treatment combined with an initial H₂O₂ concentration of 2.3 mg/L showed 1.1 to 6.5 times higher rate constants for 26 PPCPs than those for O₃ treatment alone. This was due to the contribution of OH radicals formed by the reaction of Eq. (7) [13]. However, the DEET and tetracycline rate constants did not improve despite combining the H₂O₂ and the O₃ treatment.



The rate constants of 17 PPCPs (2-QCA, acetaminophen, antipyrine, carbamazepine, clarithromycin, clenbuterol, crotamiton, DEET, fenoprofen, ifenprodil, isopropylantipyrene, mefenamic acid, metoprolol, naproxen, oxytetracycline, propranolol, and sulfamonomethoxine) increased by 1.1 to 1.6 times when an initial H₂O₂ concentration of 11.2 mg/L was combined with the O₃ treatment. In particular, even slightly lower rate constants than for the O₃ treatment alone were observed in four PPCPs such as cyclophosphamide, disopyramide, tetracycline, and theophylline. Moreover, the average rate constants of the 28 PPCPs for 2.3 mg/L and 11.2 mg/L were 6.2×10^{-3} /sec and 5.1×10^{-3} /sec, respectively, indicating that a higher H₂O₂ concentration does not necessarily lead to a faster PPCP reaction. The one reason why a high H₂O₂ concentration cannot ensure a fast reaction with the target compound is the consumption of OH radicals formed during O₃ treatment by excess H₂O₂. OH radicals can be scavenged by H₂O₂ in water as shown in Eq. (8) [13], leading to a low degradation rate of the target compounds.



When a high initial H₂O₂ concentration of 11.2 mg/L was added, OH radicals formed by the reaction of Eq. (7) were scavenged by excess H₂O₂ added during the O₃ treatment; thus, lower rate constants than those for O₃/H₂O₂ treatment using low H₂O₂ concentration of 2.3 mg/L were obtained. This result indicates that it will be important to determine the appropriate H₂O₂ dose for O₃ treatment to improve reaction rates of PPCPs by adding H₂O₂ during O₃ treatment.

4. Conclusions

This study investigated the effects of adding H₂O₂ and UV on the degradation of 30 PPCPs during O₃ treatment. The new findings from this study are as follows:

- 1) Degradation reactions of the target PPCPs with O₃, O₃/H₂O₂, and O₃/UV could be expressed by pseudo-first-order kinetics.
- 2) The combination of UV or H₂O₂ with O₃ promoted the degradation reactions of all PPCPs under the tested conditions due to direct UV photodegradation or OH radicals.
- 3) Several PPCPs such as ketoprofen and diclofenac showed much higher rate constants during O₃/UV treatment than those during O₃/H₂O₂ treatment, indicating that their degradation can be attributed to direct UV photodegradation rather than OH radicals.
- 4) From a comparison of degradation efficiency, defined as the ratio of the average rate constant (/sec) for all PPCPs to the O₃ consumption per reactor volume (mg/L), the highest degradation efficiency was obtained at an O₃ feed rate of 0.3 mg/L/min during O₃ treatment. In contrast, an O₃ feed rate of 0.15 mg/L/min produced optimum degradation efficiency during O₃/UV treatment. This result indicates that the O₃ dose required for PPCP degradation by O₃ can be reduced by combining it with UV.
- 5) PPCP degradation by O₃ was promoted by adding H₂O₂ during the O₃ treatment. However, when a high initial H₂O₂ concentration was added during the O₃ treatment, formed OH radicals were likely to be scavenged by excess H₂O₂, leading to low PPCP degradation. Therefore, it is important to determine the appropriate H₂O₂ dosage during O₃ treatment to improve PPCP degradation by adding H₂O₂ during O₃ treatment.

Acknowledgments

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