chemengineering

MDPI

Article

Effect of O_3 Dose on the O_3/UV Treatment Process for the Removal of Pharmaceuticals and Personal Care Products in Secondary Effluent

N. Evelin Paucar [1,*], IIho Kim [2], Hiroaki Tanaka [3] and Chikashi Sato [4]

[1] Department of Civil and Environmental Engineering, Idaho State University, 921 S. 8th Ave., Stop 8060, Pocatello, ID 83209, USA
[2] Department of Construction Environment Engineering, Environmental and Plant Engineering Institute, Korea Institute of Civil Engineering and Building Technology, University of Science & Technology/Senior Researcher, (Daehwa-Dong 2311) 283, Goyangdae-ro Ilsanseo-gu, Goyang-si, Kyonggi-do 411-712, Korea; jhkim@kict.re.kr
[3] Research Center for Environmental Quality Management, Graduate School of Engineering, Kyoto University, 1-2 Yumihama, Otsu, Shiga 520-0811, Japan; htanaka@biwa.eqc.kyoto-u.ac.jp
[4] Department of Civil and Environmental Engineering, Idaho State University, 921 S. 8th Ave., Stop 8060, Pocatello, ID 83209, USA; satochik@isu.edu
* Correspondence: paucnori@isu.edu

Received: 28 February 2019; Accepted: 27 May 2019; Published: 1 June 2019

Abstract: A municipal wastewater treatment plant (WWTP) is a melting pot of numerous pharmaceuticals and personal care products (PPCPs) together with many other substances. The removal of PPCPs using advanced oxidation processes within a WWTP is one way to reduce the amount of PPCPs that potentially enter an aquatic environment. The aim of this study was to examine the effectiveness of the ozone (O_3)/UV treatment process, especially, the effects of O_3 dose and reaction time, on the removal of PPCPs in the secondary effluent of a WWTP. Experiments were conducted using a pilot-scale treatment process that consisted of two flow-through reactors connected in series. Each reactor was equipped with three 65 W lamps (UV_{65W}). The experimental variables were ozone dosage (1, 2, 3, 4, and 6 mg L^{-1}) and hydraulic retention time (HRT; 5 and 10 min). On the basis of the PPCP concentrations after O_3/UV_{65W} treatment and their limit of detection (LOD), 38 PPCPs detected in the secondary effluent were classified into 5 groups ranging from the category of "sensitive" to O_3/UV_{65W} or "unstable" in the O_3/UV_{65W} process to the category of "insensitive" to O_3/UV_{65W} or "very stable" in the O_3/UV_{65W} process.

Keywords: ozone; UV; pharmaceuticals; personal care products; wastewater; advanced oxidation process

1. Introduction

In modern societies, numerous kinds of personal care products (PPCPs) are being consumed in large quantities [1], and the usage of PPCPs will likely continue to rise in the future. Although certain types of PPCPs are degraded via human/animal metabolism or decomposed quickly in the environment, other types of PPCPs are recalcitrant and maintain their biologically active properties after being excreted from a body and disposed of into a wastewater treatment system [2,3]. A wide range of PPCPs found in the aquatic environment are mainly originated from wastewater treatment plants (WWTPs) [4–7]. Because most public WWTPs are not equipped with processes to remove biorecalcitrant PPCPs [8–11], these compounds are likely discharged into receiving water bodies [8–10,12,13]. For example, sulfamethoxazole (antibiotic), carbamazepine (anticonvulsant), bezafibrate (lipid-modifying agent), clofibric acid (lipid-modifying agent) are commonly found in municipal wastewater effluent around the world [13–15]. Erythromycin is

one of the most frequently detected antibiotics in the environment [13–20]. The removal of PPCPs at WWTPs has been considered as a way to reduce the amount of PPCPs that potentially enter the aquatic environment [21].

Advanced oxidation processes (AOPs) can produce highly reactive free radicals such as hydroxyl radicals (·OH); thus, AOPs have the potential to decompose biorecalcitratnt PPCPs present in water and wastewater [22]. In the AOPs, hydroxyl radicals are the primary oxidants that attack and decompose organic compounds (their characteristics and effectiveness are described elsewhere [23]). Among various AOPs, UV photolysis, ozonation, and their combination are potential technologies capable of destroying organic pollutants in water and wastewater [21,24–27].

Ozone (O_3) has been successfully employed for the disinfection and decomposition of dissolved organic pollutants [21,24–27]. Several studies have shown that ozonation could effectively remove certain PPCPs [9,14,17,21,28–30]. The study by Park et al. [31], however, showed that a higher ozone dose (4–8 mg L^{-1}) was required for PPCP removal as compared to the dose (1–1.5 mg L^{-1}) applied for disinfection. Although UV light at λ = 254 nm has been applied for the disinfection of water and wastewater [32], it was shown to be ineffective for the direct photolysis of organic compounds that have a low quantum yield and small molar absorption coefficient [33]. In water and wastewater, UV photolysis of O_3 generates ·OH [34–36], which can mineralize various pollutants to CO_2, H_2O, and inorganic compounds, or at least, more innocuous products [37]. Ozone has the molar absorption coefficient (ε) of 2952 mol^{-1} dm^3 cm^{-1} at 254 nm UV [38], which is sufficient to generate ·OH in an aqueous solution. Therefore, the O_3/UV method has the potential to enhance the generation of ·OH [39,40]) and subsequently degrade organic pollutants [33].

Past studies on the combination of O_3 and UV focused mainly on the dosages of ozone and UV [11,41,42]. In the present study, the effects of reaction time (hydraulic retention time, HRT) in addition to the ozone dosage, were comparatively examined using a pilot-scale O_3/UV reactor process. The results suggested that the reaction time, in addition to the O_3 dosage, is an important factor to be considered in designing an O_3/UV process and that the O_3/UV treatment has the potential to remove a wide range of PPCPs from the secondary effluent of a WWTP. Furthermore, the PPCPs detected in secondary effluent were grouped on the basis of their degradability in the O_3/UV process. These PPCPs were divided into five categories ranging from the group of "sensitive" to O_3/UV or "unstable" in the O_3/UV process to the group of "insensitive" to O_3/UV or "very stable" in the O_3/UV process. A pilot-scale process used in this study provided a better understanding of the effects of O_3 on the O_3/UV process for the degradation of PPCPs present in the secondary effluent of a municipal WWTP.

2. Methodology

2.1. Experimental Setting and Operational Conditions

A pilot-scale flow-through O_3/UV process was designed in order to evaluate the removal of PPCPs found in the secondary effluent of a WWTP (Figure 1). The reactors (Metawater Co. Ltd., Tokyo, Japan) were constructed to model actual UV reactors. The experimental system consisted of a sand filtration unit (for pretreatment), feed units (a feed wastewater tank and a feed pump), two identical stainless steel O_3/UV reactors (R_1 and R_2), an ozone generator, and a tank for receiving the treated wastewater. Two UV reactors were connected in series, each having an effective volume of 35 L (189.9 cm length, 15.5 cm I.D.). The UV source was a 65 W low-pressure mercury UV lamp (UV_{65W}) with λ = 254 nm. The UV_{65W} lamp exhibited the UV output of 21.8 W and the UV irradiance of 1.025 mW/cm^2. Each UV reactor was equipped with three UV lamps. The wastewater flow rate was set at 7 L min^{-1} to give the hydraulic retention time (HRT) of 5 min per reactor, that was a total of 10 min with two UV reactors in series.

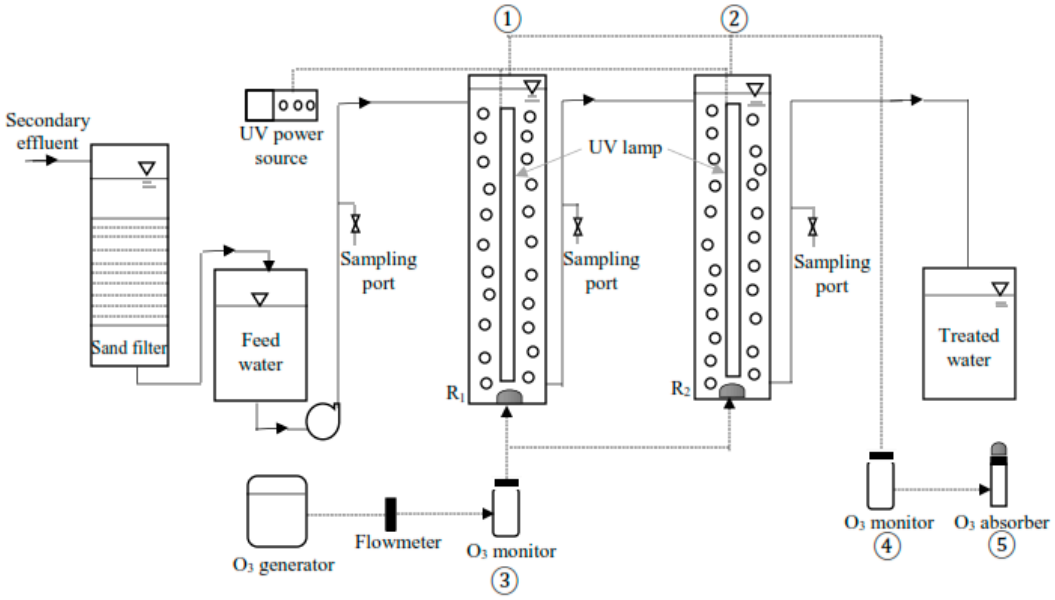

Figure 1. Schematic diagram of the experimental process.

Ozone gas was continuously supplied from the bottom of each UV reactor at a flow rate of 0.5 L min^{-1}. As is illustrated in Figure 1, the concentration of ozone in the inlet gas $(C_{O3})_{in}$, was measured by an ozone monitor (③). The gas trapped in the top of the UV reactor was released through a pipeline (① and ② dotted line), and the concentrations of ozone (O_3) in the exit gas, $(C_{O3})_1$ and $(C_{O3})_2$) were measured by an ozone monitor (④) located in front of an ozone absorber (⑤). The ozone dose, which was the amount of O_3 directed from the ozone generator to the unit volume of water to be treated, was calculated using the following equation [30,43,44]:

$$[\text{Ozone Dose}] = (C_{O3})_{in}\left(\frac{Q_{O_3}}{Q_{WW}}\right) \quad (1)$$

where [Ozone Dose] is the applied ozone dose (mg dm^{-3} or mg L^{-1}), $(C_{O3})_{in}$ is the ozone concentration in the gas stream at the inlet or the feed gas, Q_{O3} is the feed ozone flow rate (dm^3min^{-1} or $Lmin^{-1}$), and Q_{WW} is the wastewater flow rate (dm^3min^{-1} or $Lmin^{-1}$). For the two reactors in series, the total ozone dose was calculated by adding the ozone dose of the two reactors. Because the concentrations of ozone in the exit gas, $(C_{O3})_1$ and $(C_{O3})_2$, were about 1/10 of $(C_{O3})_{in}$, the ozone losses in the process were considered minimal.

2.2. Experimental Procedure

Three different runs (Run 1, 2, and 3) were carried out with the injection O_3 concentration $(C_{O3})_{in}$ of 14 mg L^{-1}, 28 mg L^{-1}, and 42 mg L^{-1}, respectively, in each reactor. As presented in Table 1, the experiments were conducted with these values of the two variables: (i) applied ozone doses of 1, 2, 3, 4, and 6 mg L^{-1}), and (ii) reaction time or HRT of 5 and 10 min. Note that the reactor 1 (R_1) in run 2 and the reactor 2 (R_2) in Run 1 gave the same ozone dose of 2 mg L^{-1}.

Table 1. Ozone dose applied to the O_3/UV_{65W} reactors.

Run	Injected O_3 Concentration (mg L^{-1})	O_3 Dose per UV Reactor (mg L^{-1})	
		R_1 HRT (R_1) = 5 min	R_2 HRT (R_1 + R_2) = 10 min
1	14	1	2
2	28	2	4
3	42	3	6

R_1: Reactor 1; R_2: Reactor 2.

The feed secondary effluent was obtained from a conventional activated sludge WWTP in Shiga, Japan, which had the following characteristics: pH ranging from 6.5 to 6.8, dissolved organic carbon (DOC) concentration from 2.7 to 3.4 mg L^{-1}, and UV absorbance from 0.0514 to 0.0779 cm^{-1} at 254 nm (UV_{254}). Other wastewater parameters were typically, biochemical oxygen demand (BOD) of 200 mg L^{-1} in influent and 1.1 mg L^{-1} in effluent (before sand filtration); chemical oxygen demand (COD) of 79 mg L^{-1} in influent, 5.4–10 mg L^{-1} before sand filtration, and 4.7–9.7 mg L^{-1} after sand filtration; suspended solids (SS) of 160 mg L^{-1} in influent, <1–8 mg L^{-1} before sand filtration, and <1–4 mg L^{-1} after sand filtration; and total organic carbon (TOC) of 83 mg L^{-1} in influent [45]. The concentrations of total nitrogen in influent and effluent were estimated to be 30 and 5.6 mg L^{-1}, respectively, and those of total phosphorus in influent and effluent were estimated to be 3 and 0.06 mg L^{-1}, respectively, from the work of Tainaka, 2008 [46]. For each experimental run, the system was operated for more than three HRT before the samples were taken to obtain steady-state samples.

2.3. Sample Preparation and Analyses

From a sampling port of each reactor, 1 L of sample was collected. The sample was immediately purged with N_2 gas to remove residual O_3 to stop the reactions between O_3 and PPCPs and then analyzed for PPCPs using LC–MS/MS following the method described in the literature [47,48]. Dissolved O_3 was analyzed by the indigo method [49], in which the absorbance was measured using a spectrophotometer (UV-16000, Shimazu) at 600 nm wavelength. Other water quality parameters (TOC, DOC) were measured according to Kim et al. (2009) [47].

3. Results and Discussion

In this study, 38 PPCPs were detected in the secondary effluent of a municipal WWTP. The limit of detection (LOD) values for these 38 PPCPs are presented in Table S1, as supplemental data. The PPCPs found in the feed wastewater and the effluent of the O_3/UV reactors were examined here with respect to the ozone dose and the reaction time (HRT) in reference to their use groups. The concentrations of the PPCPs are shown on the basis of their use groups, i.e., antibiotics, analgesics, antiarrhythmic agents, anticonvulsants, vasodilators, lipid-modifying agents, and remaining PPCPs (anti-itch drugs, anti-psychotic drugs, insect repellents, bronchodilators, diuretics, peptic ulcer drugs, N-methyl-D-aspartate (NMDA) receptor antagonists, antifungal drugs, antimicrobial drugs, and antineoplastic agents) in Figures 2–7, respectively; (a), (b) and (c) in these figures refer to Runs 1, 2, and 3, respectively, and Ro, R1, and R2 refer to the feed secondary effluent, R_1 reactor (HRT = 5 min) effluent, and R_2 reactor (HRT = 10 min) effluent, respectively. The LOD of each PPCP compound is shown by the dotted line. The measured PPCP concentrations at or below their LOD (≤LOD) are not shown. The injected ozone concentrations and ozone dosages for these runs and reactors are summarized in Table 1.

The control run was carried out with UV_{65W} in the absence of O_3. In the control run, two analgesics (diclofenac and isopropylantipyrine), one antibiotic (ciprofloxacin), one lipid-modifying agent (clofibric acid), and one antimicrobial drug (chloramphenicol) were degraded to or below their LOD (≤LOD) in 5 min (R_1 reactor). Naproxen (analgesic) and nalidixic acid (antibiotic) were degraded in 10 min (R_2 reactor). These compounds appeared to be sensitive to UV.

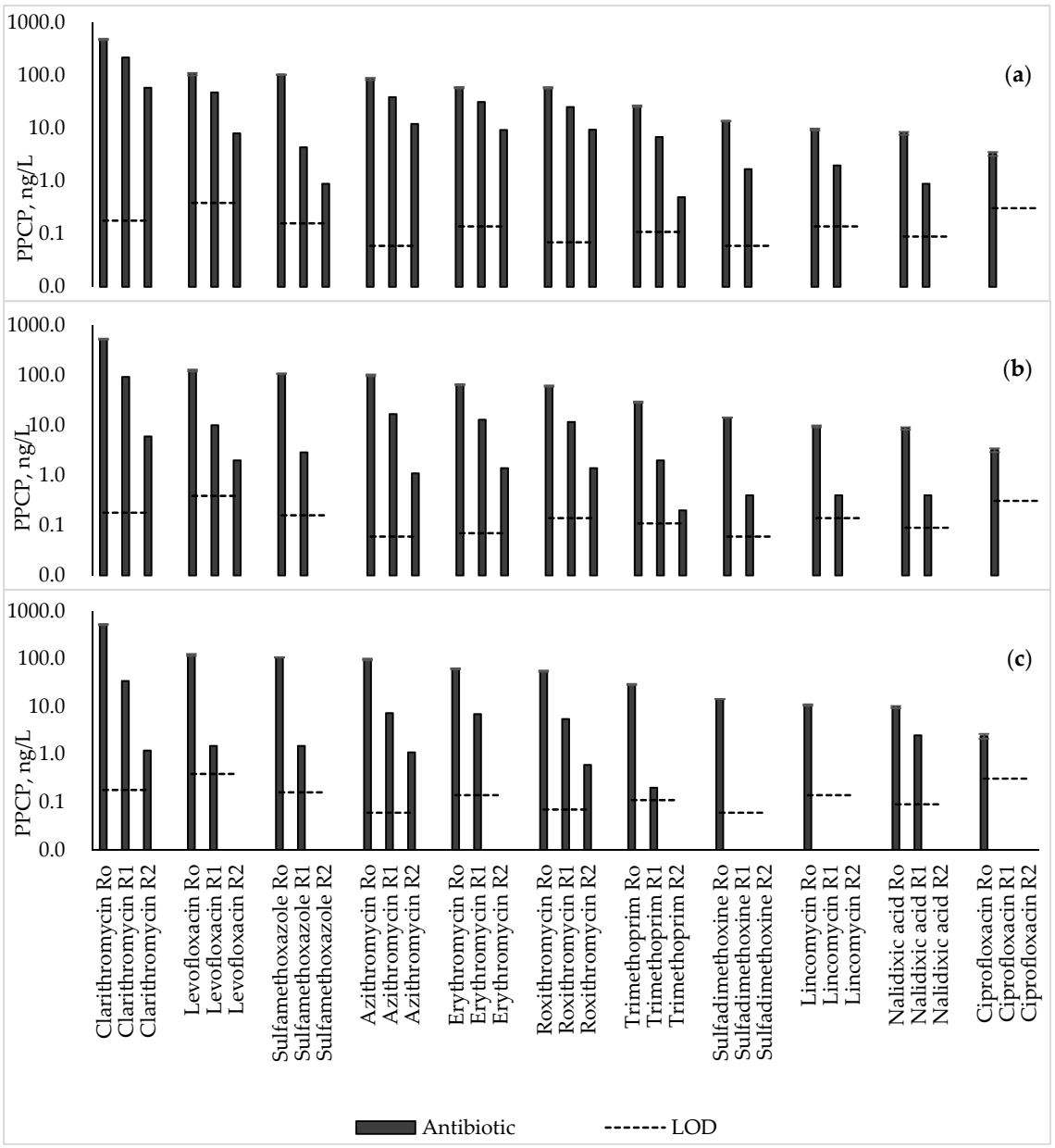

Figure 2. Concentrations of 11 antibiotics in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3. PPCP: personal care products.

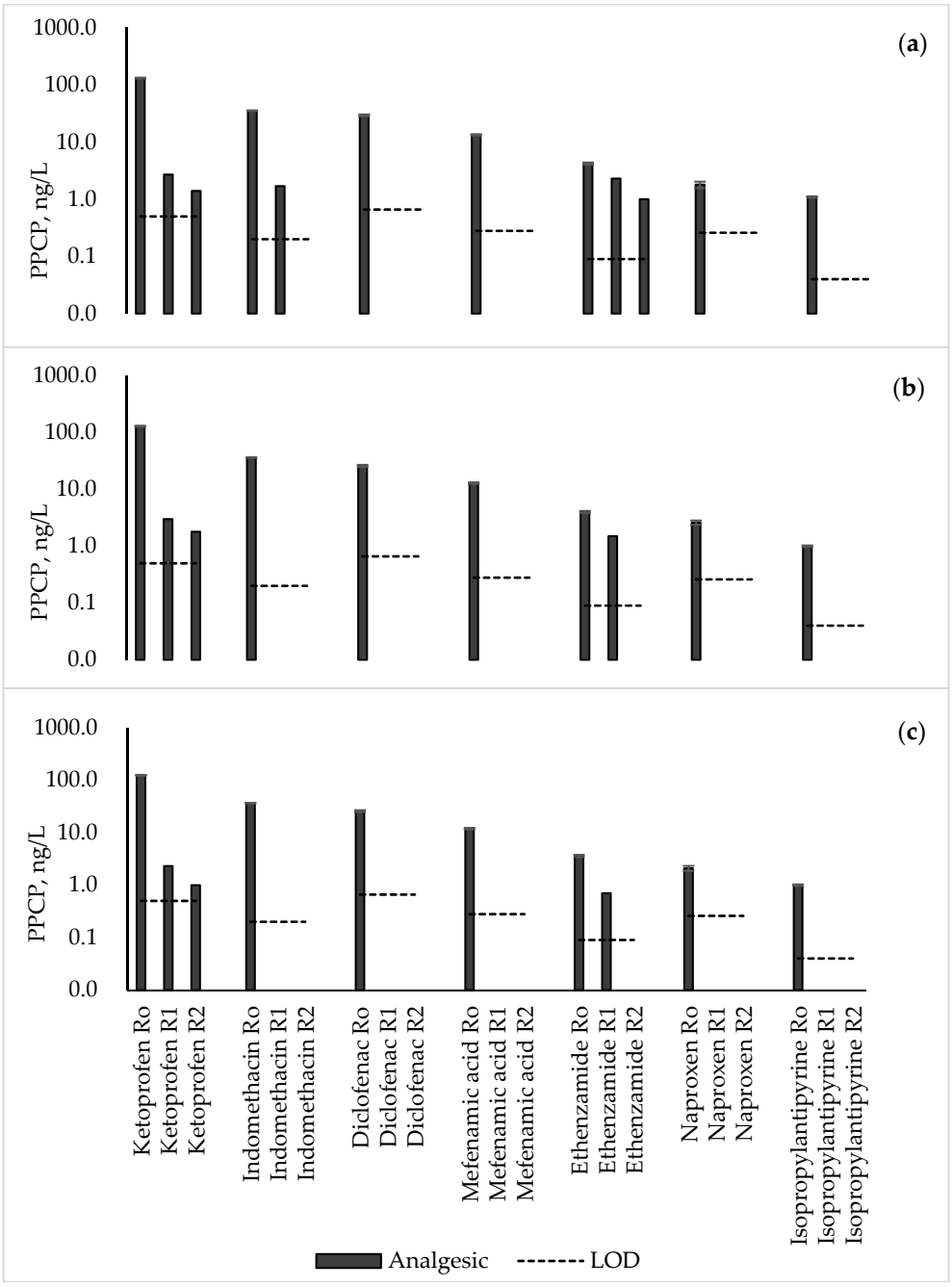

Figure 3. Concentrations of seven analgesics in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

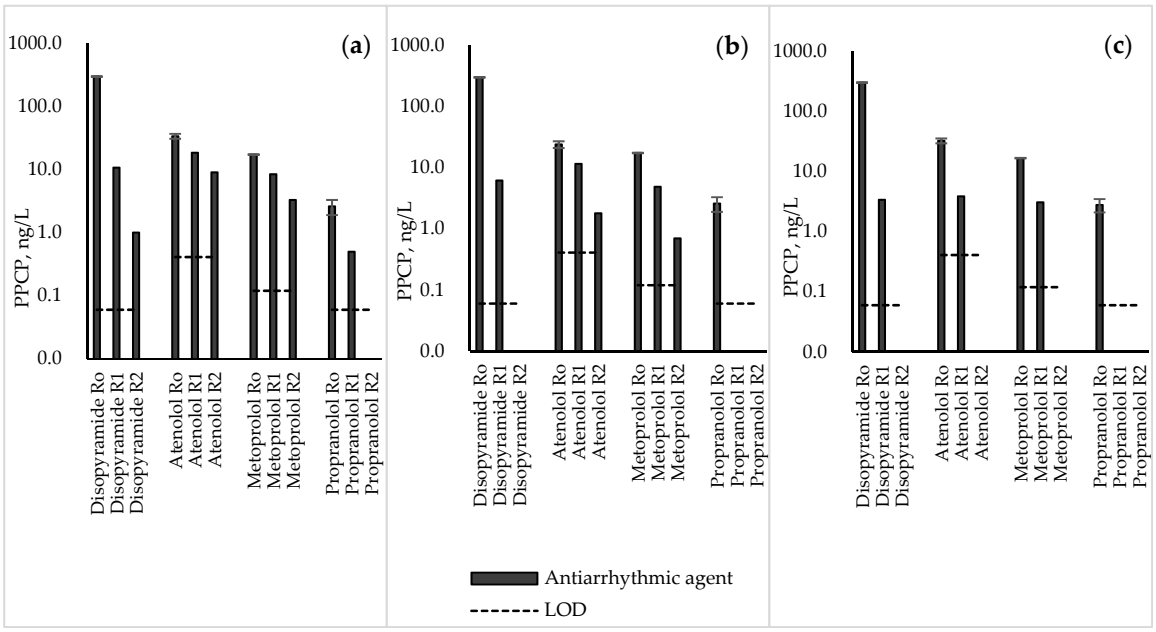

Figure 4. Concentrations of four antiarrhythmic agents in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

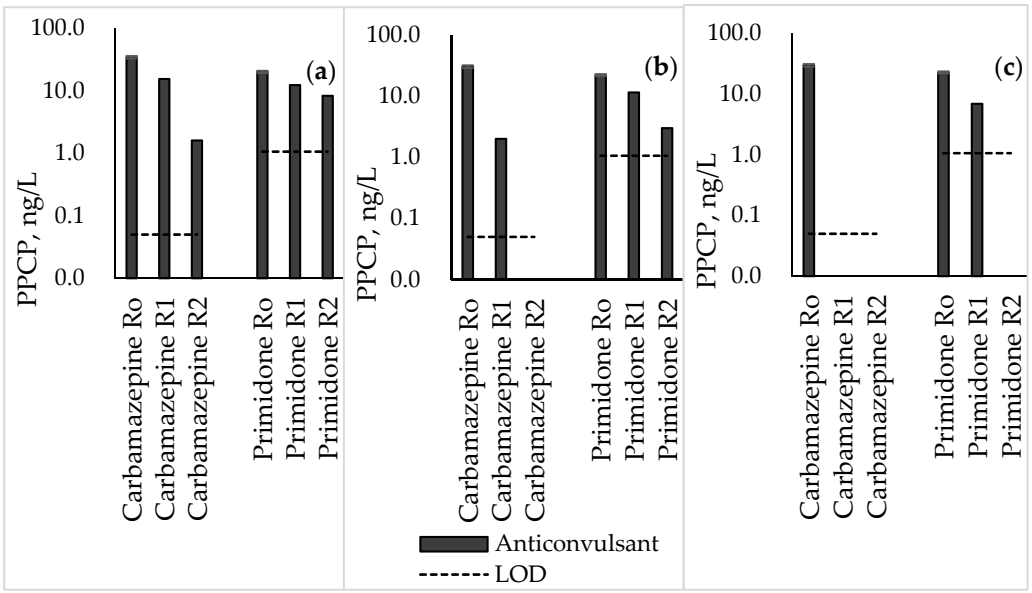

Figure 5. Concentrations of two anticonvulsants in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mgL^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

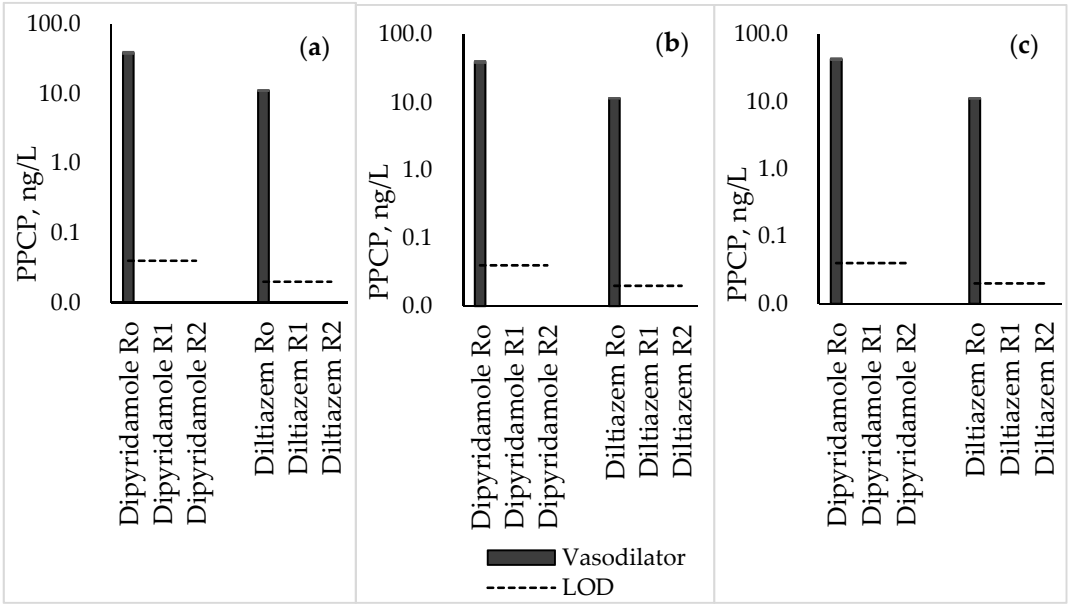

Figure 6. Concentrations of two vasodilators in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

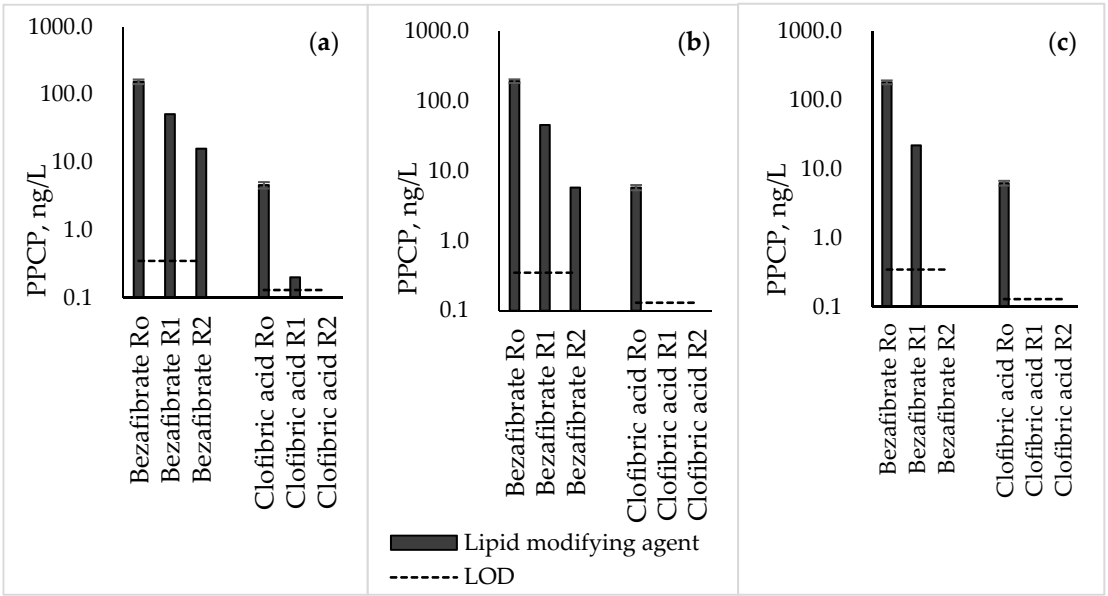

Figure 7. Concentrations of two lipid-modifying agents in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

3.1. Antibiotics

Of the 38 PPCPs detected, 11 were antibiotics (Figure 2). The mean and standard error were calculated using the feed solution (R_o) in three runs (Runs 1, 2, and 3). The results showed that 8 (ciprofloxacin, sulfadimethoxine, lincomycin, nalidixic acid, sulfamethoxazole, levofloxacin, erythromycin, and trimethoprim) out of the 11 antibiotics were degraded to or below their LOD (≤LOD) at the ozone dose of 6 mg L^{-1} in 10 min. In this O_3/UV_{65W} process, ciprofloxacin was degraded (≤LOD) at the ozone dose of 1 mg L^{-1} in 5 min in the O_3/UV_{65W} process. Note that ciprofloxacin was degraded (≤LOD) in 5 min in the control (UV only) run. In the past ozone treatment studies,

ciprofloxacin was degraded to >99% at the ozone dose of <6.2 mg L^{-1} [13] and to 83% at 3 mg L^{-1} with the contact time of 10 min [50].

In the present study, clarithromycin, azithromycin, and roxithromycin were shown to be insensitive to O_3/UV_{65W} and very stable in the O_3/UV_{65W} process. Note that these PPCPs were not degraded (≤LOD) in the control run. With the O_3-only (without UV) treatment, clarithromycin required the ozone dose of 6 mg L^{-1} and HRT of 10 min to degrade (≤LOD) [30]. In the past ozone treatment studies, roxithromycin was removed up to 73% and 84% with the ozone doses of 4 and 8 mg L^{-1}, respectively [51], and >63% removal at the ozone dose of 5 mg L^{-1} [52]. In the present study with the O_3/UV_{65W} process, roxithromycin was not degraded (≤LOD) at the O_3 dose of 6 mg L^{-1}.

Sulfadimethoxine, lincomycin, nalidixic acid, and sulfamethoxazole required the ozone doses of 2–6 mg L^{-1} to degrade to their LOD level; thus, it can be said that these compounds are slightly sensitive to O_3/UV_{65W}. In the ozone-alone study by Rosal et al. (2010) [13], lyncomycin was removed by >88% at the ozone dose of <2.4 mg L^{-1}. Since, in the O_3/UV_{65W} process, lyncomycin required the ozone dose of 2–3 mg L^{-1} to degrade (≤LOD), UV showed little effect on lyncomycin degradation by O_3. The removal of sulfamethoxazole by O_3 alone has been studied by several researchers. Their results showed sulfamethoxazole removal >92% at the ozone dose of 5 mg L^{-1} [14], >99% at 7 mg L^{-1} [53], 47% at 2 mg L^{-1}, 99% at 4 mg L^{-1}, and 100% removal at 8 mg L^{-1} [51]. Because sulfamethoxazole was degraded (≤LOD) at the ozone dose of 4 mg L^{-1} in the O_3/UV_{65W} process, UV appears to enhance the ozone treatment of sulfamethoxazole. Nalidixic acid was not degraded to ≤LOD in 5 min with or without O_3 but was degraded (≤LOD) in 10 min with or without O_3, indicating that the reaction time (not O_3) is important for the degradation of nalidixic acid.

Erythromycin and trimethoprim required the ozone dose of 6 mg L^{-1} in the R_2 reactor (HRT of 10 min) to be degraded (≤LOD); thus, they are relatively insensitive to O_3/UV_{65W} and stable in the O_3/UV_{65W} process. In the ozone treatment studies, erythromycin was degraded by 73% at the ozone dose of 4 mg L^{-1} [51], >92% at 5 mg L^{-1} [14], and >99% at 7 mg L^{-1} [53]. Past studies with ozone alone showed trimethoprim removal >85% at the ozone dose of 5 mg L^{-1} [14] and >99% at 7 mg L^{-1} [53]. In the present study, trimethoprim was degraded (≤LOD) at the ozone dose of 6 mg L^{-1} in the O_3/UV_{65W} process but it was not degraded in the control run, suggesting that O_3 affected the photo-degradation of trimethoprim.

3.2. Analgesics

Seven analgesics (diclofenac, mefenamic acid, naproxen, indomethacin, isopropylantipyrine, ethenzamide, and ketoprofen) were detected in the secondary effluent (Figure 3). Diclofenac, mefenamic acid, naproxen, and isopropylantipyrine were degraded (≤LOD) at the ozone dose of 1 mg L^{-1} in 5 min (R_1 reactor) in the O_3/UV_{65W} process. In the control run, diclofenac and isopropylantipyrine were degraded (≤LOD) in 5 min, whereas mefenamic acid, naproxen, indomethacin, ethenzamide, and ketoprofen were not degraded. The results indicated that photodegradation of mefenamic acid, naproxen, indomethacin, ethenzamide, and ketoprofen were positively affected by O_3. Naproxen was degraded in 10 min in the control run, whereas it was degraded in 5 min at the O_3 dose of 1 mg L^{-1}, showing that the photodegradation of naproxen was enhanced by O_3 in the O_3/UV_{65W} process. The high degradability of naproxen by O_3/UV was previously reported by Giri et al. [54]. Diclofenac was found to be highly susceptible to photodegradation [55,56]. Several past studies showed that diclofenac and naproxen degrade easily with O_3. Diclofenac was removed by >96% at the ozone dose of 5 mg L^{-1} [14], >99% at 2.1 mg L^{-1} [17], >98% at 7 mg L^{-1} [53], and >94% at 5 mg L^{-1} [57]. With ozone doses similar to those of the present O_3/UV_{65W} work, naproxen was removed by >96% [17,53], and similar results were reported with ozone doses of 2, 4, and 8 mg L^{-1} [51]. Relatively high degradability of isopropylantipyrine by O_3/UV has been reported by Giri et al. [54].

Indomethacin was degraded (≤LOD) at the O_3 dose of 2 mg L^{-1} in 10 min but not degraded in 10 min in the control run, indicating that O_3 enhanced the photodegradation of indomethacin. The result suggests that indomethacin is relatively sensitive to O_3/UV_{65W}. The reported degradability

of indomethacin by ozone varies. Past studies showed that indomethacin was degraded by >50% at the ozone dose of 5 mg L^{-1} [14] and >97% at <2.4 mg L^{-1} [13]. The high degradability of indomethacin by O_3/UV was reported by Giri et al. [54]. Ethenzamide was degraded (≤LOD) at the ozone dose of 4 mg L^{-1} in 10 min in the O_3/UV_{65W} process, whereas it was not degraded in the control run, suggesting that O_3 affected the photodegradation of ethenzamide. The results indicated ethenzamide is slightly sensitive to O_3/UV_{65W}. Ketoprofen was not degraded (≤LOD) in the control and in the O_3/UV_{65W} run with a dose as high as 6 mg L^{-1} in 10 min. The result suggested that ketoprofen is insensitive to UV_{65W} and O_3/UV_{65W}. In the studies with ozone, ketoprofen was removed by 11% at the ozone dose of 2 mg L^{-1} [51], 73% at 3 mg L^{-1} [58], and up to 98% at 16.3 mg L^{-1} [13]. It seems that considerably high doses of UV and O_3 are required to completely destroy ketoprofen in wastewater.

3.3. Antiarrhythmic Agents

Four antiarrhythmic agents (propranolol, disopyramide, atenolol, and metoprolol) were detected in the secondary effluent (Figure 4). These PPCPs were not degraded (≤LOD) in the control run. In the O_3/UV_{65W} process, propranolol was degraded (≤LOD) at the O_3 dose of 2 mg L^{-1} in 10 min, showing it is relatively sensitive to O_3/UV_{65W}. Disopyramide required the O_3 dose of 2–6 mg L^{-1} to be degraded (≤LOD), indicating it is slightly sensitive to O_3/UV_{65W}. On the other hand, atenolol and metoprolol required the O_3 dose of 6 mg L^{-1} and the HRT of 10 min to be degraded (≤LOD), suggesting they are relatively insensitive to O_3/UV_{65W}.

3.4. Anticonvulsants

Carbamazepine and primidone are the only two anticonvulsants detected in the secondary effluent (Figure 5). Neither PPCP was degraded (≤LOD) in the control run. In the O_3/UV_{65W} process, carbamazepine was degraded (<LOD) at the ozone dose of 3 mg L^{-1} in 5 min, showing that O_3 enhanced the photodegradation of carbamazepine. In the studies with ozone alone, carbamazepine was degraded by >98% at the ozone dose of 5 mg L^{-1} [14,57], >99% at 7 mg L^{-1} [53], and 99% at 4 and 8 mg L^{-1} [51]. It is noteworthy that Giri et al. [54] reported that the degradability of carbamazepine decreased in their O_3/UV process as compared to the O_3-only process due to a negative impact of UV. Primidone required the ozone dose of 6 mg L^{-1} and the HRT of 10 min to be degraded (≤LOD), indicating primidone is relatively insensitive to O_3/UV_{65W}.

3.5. Vasodilators

Two vasodilators (dipyridamole and diltiazem) were detected in the secondary effluent (Figure 6). Neither PPCP was degraded (≤LOD) in the control run. In the O_3/UV_{65W} process, dipyridamole and diltiazem were degraded (≤LOD) at the O_3 dose of 1 mg L^{-1} in 5 min, showing that the photodegradation of these PPCPs was enhanced by O_3.

3.6. Lipid-Modifying Agents

Two lipid-modifying agents (bezafibrate and clofibric acid) were detected (Figure 7).

Bezafibrate is relatively insensitive to O_3/UV_{65W}, requiring the O_3 dose of 6 mg L^{-1} and the HRT of 10 min to be degraded (≤LOD). Bezafibrate was not degraded (≤LOD) in the control run. In the past studies with ozone alone, bezafibrate removal efficiencies of 49% and >99% were observed at the ozone doses of 2 and 5 mg L^{-1}, respectively [21], up to 87% at 7.5 mg L^{-1} [52], and 97% at 16.3 mg L^{-1} [13]. Clofibric acid was degraded (≤LOD) at the ozone dose of 2 mg L^{-1} in 5 min in the O_3/UV_{65W} process. Note that clofibric acid was degraded (≤LOD) in the control run but it was detected at the level very close to its LOD in the effluent of the R_1 reactor at the O_3 dose of 1 mg L^{-1} in Run 1 (O_3/UV_{65W} run). In an ozone-alone study, clofibric acid was removed by 50% at the O_3 dose of 5 mg L^{-1} [14]. Clofibric acid was shown to be relatively sensitive to UV and O_3/UV_{65W}.

3.7. Other PPCPs

The 10 remaining PPCPs found in the secondary effluent were crotamiton, sulpiride, N,N-diethyl-3-methylbenzamide (DEET), theophylline, furosemide, pirenzepine, ifenprodil, griseofulvin, chloramphenicol, and cyclophosphamide, which are an anti-itch drug, anti-psychotic drug, insect repellent, bronchodilator, diuretic, peptic ulcer drug, NMDA receptor antagonist, antifungal drug, antimicrobial drug, and antineoplastic agent, respectively (Figure 8). All of these PPCPs, except for chloramphenicol, were not degraded (≤LOD) in the control run. Cloramphenicol was degraded (≤LOD) in the control run and also in the O_3/UV_{65W} run at the ozone dose of 1 mg L^{-1} in 5 min, showing that chloramphenicol is very susceptible to UV and O_3/UV_{65W}. Furosemide was degraded (≤LOD) at the ozone dose of 2 mgL^{-1} in 10 min (R_2 reactor), indicating that furosemide is relatively sensitive to O_3/UV_{65W}. Pirenzepine, ifenprodil, and griseofulvin required the O_3 dose of 2–6 mgL^{-1} to be degraded (≤LOD), showing these PPCPs are slightly sensitive to O_3/UV_{65W}. Crotamiton and cyclophosphamide were degraded (≤LOD) at 6 mg L^{-1} in 10 min (R_2 reactor), indicating that these compounds are relatively insensitive to O_3/UV_{65W}. On the other hand, sulpiride, DEET, and theophylline resisted to O_3/UV_{65W}. These compounds were not degraded (≤LOD) in 10 min at the ozone dose of 6 mgL^{-1}, the largest dose applied in this study.

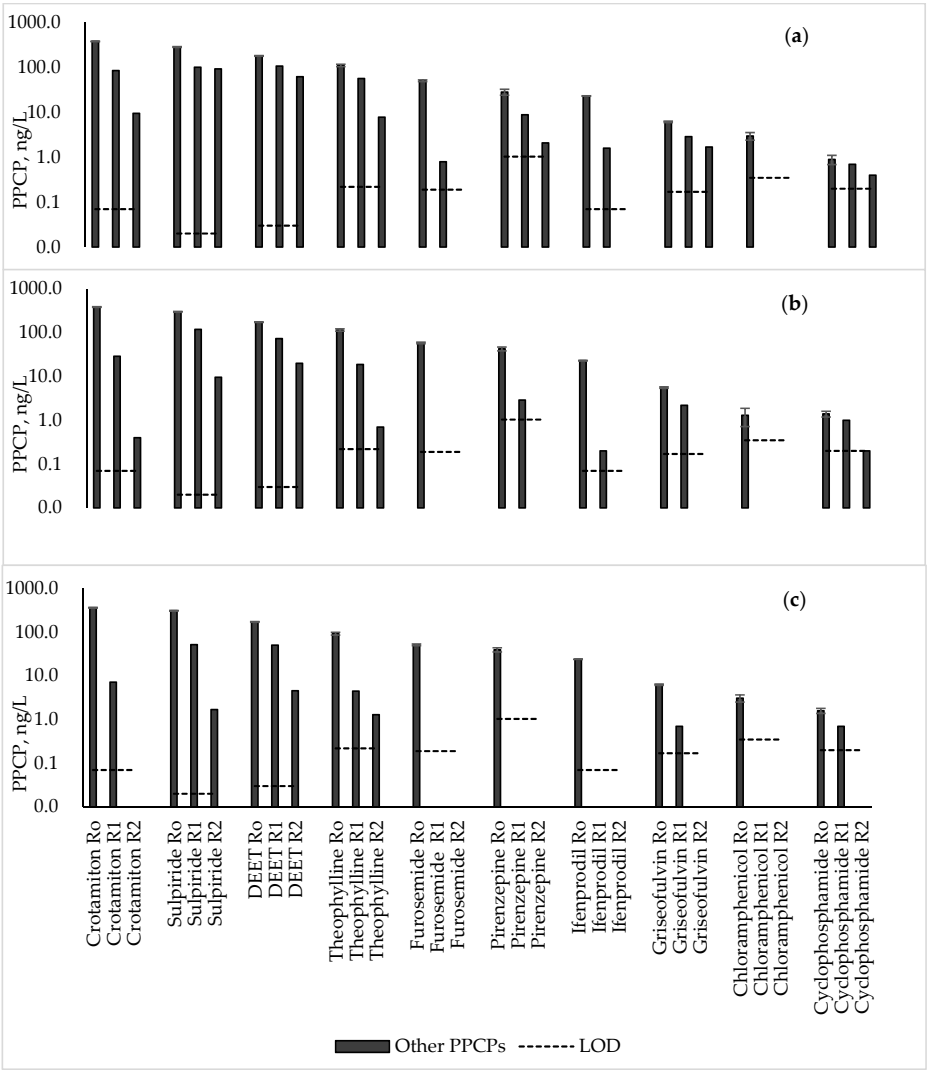

Figure 8. Concentrations of 10 other PPCPs in the feed secondary effluent (R_o) and effluent of the R_1 and R_2 reactors at the O_3 doses of: (**a**) 1 and 2 mg L^{-1}, respectively, in Run 1; (**b**) 2 and 4 mg L^{-1}, respectively, in Run 2; and (**c**) 3 and 6 mg L^{-1}, respectively, in Run 3.

3.8. Relative Degradability

Figure 9 shows the relative degradability of 38 PPCPs detected in the secondary effluent. In this figure, the relative degradability was grouped on the basis of the compounds' concentrations after the O_3/UV_{65W} treatment and their corresponding LOD, i.e., above or below their LOD. The shaded area indicates that the PPCP was degraded to or below its LOD (≤LOD). The degradability of the PPCPs was classified into five main groups: (i) "sensitive" to O_3/UV_{65W} or "unstable" in the O_3/UV_{65W} process, (ii) "relatively sensitive" to O_3/UV_{65W} or "relatively unstable" in the O_3/UV_{65W} process, (iii) "slightly sensitive" to O_3/UV_{65W} or "relatively stable" in the O_3/UV_{65W} process, iv) "relatively insensitive" to O_3/UV_{65W} or "stable" in the O_3/UV_{65W} process, and v) "insensitive" to O_3/UV_{65W} or "very stable" in the O_3/UV_{65W} process [30]. Of 38 PPCPs detected in the secondary effluent, 8 PPCPs were classified into the "sensitive/unstable" group, including dipyridamole, diclofenac, mefenamic acid, diltiazem, ciprofloxacin, chloramphenicol, naproxen, and isopropylantipyrine. Of the eight "sensitive/unstable" PPCPs, four (diclofenac, mefenamic acid, naproxen, and isopropylantipyrine) were analgesics, and two (dipyridamole and diltiazem) were vasodilators. These PPCPs were degraded (≤LOD) at the O_3 dose of 1 mg L^{-1} in 5 min.

Furosemide, indomethacin, clofibric acid, and propranolol were classified into the group of "relatively sensitive" to O_3/UV_{65W} and "relatively unstable" in the O_3/UV_{65W} process. These PPCPs were degraded (≤LOD) at the O_3 dose of 2 mg L^{-1} in 10 min. The PPCPs in the group of "relatively insensitive" to O_3/UV_{65W} and "stable" in the O_3/UV_{65W} process were crotamiton, bezafibrate, levofloxacin, erythromycin, atenolol, trimethoprim, primidone, metoprolol, and cyclophosphamide. These PPCPs required the ozone dose of 6 mg L^{-1} to be degraded (≤LOD). The PPCPs classified into the group of "insensitive" to O_3/UV_{65W} and "very stable" in the O_3/UV_{65W} process were clarithromycin, sulpiride, DEET, ketoprofen, theophylline, azithromycin, and roxithromycin. These PPCPs were not degraded (≤LOD) in 10 min at the ozone dose as high as 6 mg L^{-1}.

The group of "slightly sensitive" to O_3/UV_{65W} or "relatively stable" in the O_3/UV_{65W} process included all the remaining PPCPs. These PPCPs required the ozone doses of 2–6 mg L^{-1} to be degraded (≤LOD).

Noting that the ozone dose of 2 mg L^{-1} occurred in the R_2 reactor (HRT = 10 min) in Run 1 and also in the R_1 reactor (HRT = 5 min) in Run 2 (Table 1), a comparison was made in terms of the effects of the reaction time (HRT) on the degradability of the PPCPs. At the same O_3 dosage (2 mg L^{-1}), sulfadimethoxine, lincomycin, ifenprodil, and nalidixic acid were not degraded in 5 min but were degraded (≤LOD) in 10 min, showing that sulfadimethoxine, lincomycin, ifenprodil, and nalidixic required a longer reaction time (>5 min).

The AOP treatment efficiency relies heavily on the chemical properties of contaminants and on the operating conditions [59]. The decomposition of PPCPs by AOPs depends on a number of factors, for example, the oxidant dosage, the concentrations of PPCPs, the mode of the AOP operation, and water quality. Natural organic compounds such as carbonate, bicarbonate, chlorine ions are known to act as radical scavengers. Because these compounds compete with target pollutants for hydroxyl radicals, their presence increases oxidant demands and lowers treatment efficiency [60]. Although the O_3/UV_{65W} treatment is a promising technology for the removal of a wide range of PPCPs from secondary effluent, further comprehensive understanding is needed in the areas of the reaction kinetics, decomposition pathways, formation of byproducts, and toxicity of wastewater treated by the O_3/UV_{65W} process.

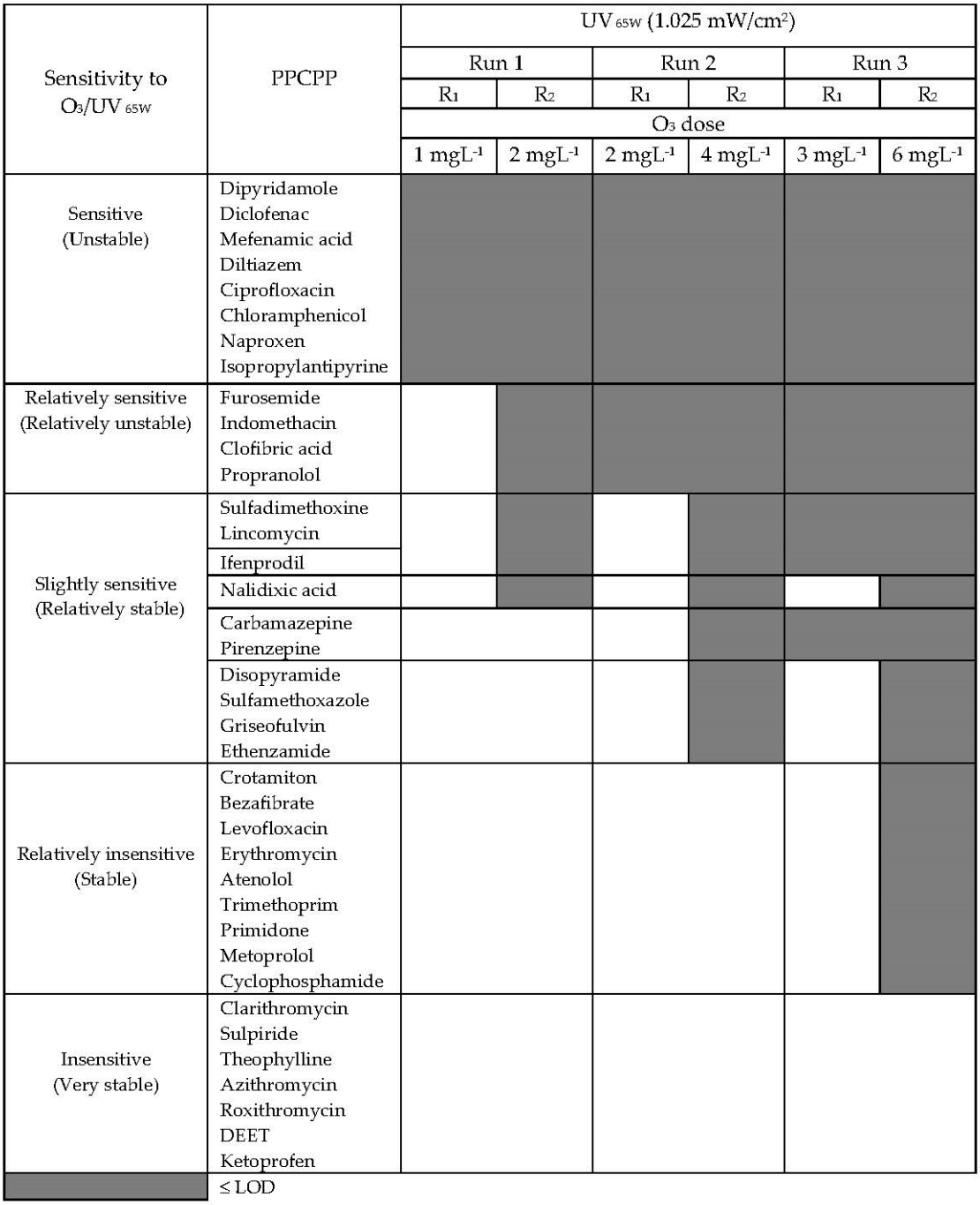

Figure 9. Degradability of 38 PPCPs in the two flow-through O_3/UV_{65W} reactors in series (R_1, R_2).

4. Conclusions

The effects of O_3 dose and reaction time on the O_3/UV_{65W} treatment process were investigated for the removal of PPCPs in the secondary effluent of a WWTP. The experimental variables were the injected O_3 concentration (14, 28, and 42 mg L^{-1}), the ozone dosage (1, 2, 3, 4, and 6 mg L^{-1}), and the reaction time (HRT, 5 and 10 min). Among 38 PPCPs detected in the secondary effluent, 31 PPCPs were degraded to or below their LOD (≤LOD) at the O_3 dosage of 6 mg L^{-1} in 10 min. Of these, eight PPCPs, including dipyridamole, diclofenac, mefenamic acid, diltiazem, ciprofloxacin, chloramphenicol, naproxen, and isopropylantipyrine, were readily degrade (≤LOD) at the O_3 dose of 1 mg L^{-1} in 5 min, and seven PPCPs, including clarithromycin, sulpiride, DEET, ketoprofen, theophylline, azithromycin,

and roxithromycin, were not degraded (≤LOD) at the ozone dosage of 6 mg L^{-1} with the HRT of 10 min.

The 38 PPCPs detected in the secondary effluent were classified into 5 groups according to their degradability: (i) "sensitive" to O_3/UV_{65W} or "unstable" in the O_3/UV_{65W} process; (ii) "relatively sensitive" to O_3/UV_{65W} or "relatively unstable" in the O_3/UV_{65W} process; (iii) "slightly sensitive" to O_3/UV_{65W} or "relatively stable" in the O_3/UV_{65W} process; (iv) "relatively insensitive" to O_3/UV_{65W} or "stable" in the O_3/UV_{65W} process; and (v) "insensitive" to O_3/UV_{65W} or "very stable" in the O_3/UV_{65W} process. The results from this study suggest that O_3/UV_{65W} treatment has the potential to remove a wide range of PPCPs from the secondary effluent of a WWTP.

Supplementary Materials: The following is available online at http://www.mdpi.com/2305-7084/3/2/53/s1, Table S1: Use and name of PPCPs detected in tested water.

Author Contributions: N.E.P. was responsible for analyzing data and writing the manuscript; I.K. for carrying out the experiments; H.T. and C.S. for advising, coordinating, and editing the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Suárez, S.; Carballa, M.; Omil, F.; Lema, J.M. How are pharmaceutical and personal care products (PPCPs) removed from Urban Wastewaters? *Rev. Environ. Sci. Biotechnol.* **2008**, *7*, 125–138. [CrossRef]
2. United States Environmental Protection Agency. Pharmaceuticals and Personal Care Products (PPCPs). 2011. Available online: http//epa.gov/ppcp (accessed on 26 May 2016).
3. Westerhoff, P.; Yoon, Y.; Snyder, S.; Wert, E. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.* **2005**, *39*, 6649–6663. [CrossRef]
4. Daughton, C.G.; Ternes, T.A. Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Perspect.* **1999**, *107*, 167–176. [CrossRef]
5. Dickenson, E.R.V.; Snyder, S.A.; Sedlak, D.L.; Drewes, J.E. Indicator compounds for assessment of wastewater effluent contributions to flow and water quality. *Water Res.* **2011**, *45*, 1199–1212. [CrossRef] [PubMed]
6. Huang, Q.; Yu, Y.; Tang, C.; Zhang, K.; Cui, J.; Peng, X. Occurrence and behavior of non-steroidal anti-inflammatory drugs and lipid regulators in wastewater and urban river water of the Pearl River Delta, South China. *J. Environ. Monit.* **2011**, *13*, 855–863. [CrossRef]
7. Zhou, J.L.; Zhang, Z.L.; Banks, E.; Grover, D.; Jiang, J.Q. Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water. *J. Hazard. Mater.* **2009**, *166*, 655–661. [CrossRef] [PubMed]
8. Halling-Sørensen, B.; Nors Nielsen, S.; Lanzky, P.F.; Ingerslev, F.; Holten Lützhøft, H.C.; Jørgensen, S.E. Occurrence, fate and effects of pharmaceutical substances in the environment—A review. *Chemosphere* **1998**, *36*, 357–393. [CrossRef]
9. Huber, M.M.; Canonica, S.; Park, G.Y.; von Gunten, U. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **2003**, *37*, 1016–1024. [CrossRef]
10. Petrović, M.; Hernando, M.D.; Díaz-Cruz, M.S.; Barceló, D. Liquid chromatography-tandem mass spectrometry for the analysis of pharmaceutical residues in environmental samples: A review. *J. Chromatogr. A* **2005**, *1067*, 1–14. [CrossRef] [PubMed]
11. Sui, Q.; Huang, J.; Lu, S.; Deng, S.; Wang, B.; Zhao, W.; Qiu, Z.; Yu, G. Removal of pharmaceutical and personal care products by sequential ultraviolet and ozonation process in a full-scale wastewater treatment plant. *Environ. Sci. Eng.* **2014**, *8*, 62–68. [CrossRef]
12. Radjenović, J.; Petrović, M.; Barceló, D. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. *Water Res.* **2009**, *43*, 831–841. [CrossRef]
13. Rosal, R.; Rodríguez, A.; Perdigón-Melón, J.A.; Petre, A.; García-Calvo, E.; Gómez, M.J.; Agüera, A.; Fernández-Alba, A.R. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res.* **2010**, *44*, 578–588. [CrossRef] [PubMed]

14. Ternes, T.A.; Stüber, J.; Herrmann, N.; McDowell, D.; Ried, A.; Kampmann, M.; Teiser, B. Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res.* **2003**, *37*, 1976–1982. [CrossRef]
15. Hollender, J.; Zimmermann, S.G.; Koepke, S.; Krauss, M.; McArdell, C.S.; Ort, C.; Singer, H.; von Gunten, U.; Siegrist, H. Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. *Environ. Sci. Technol.* **2009**, *43*, 7862–7869. [CrossRef]
16. Monteiro, S.C.; Boxall, A.B.A. Occurrence and fate of human pharmaceuticals in the environment. *Rev. Environ. Contam. Toxicol.* **2010**, *202*, 53–154. [PubMed]
17. Snyder, S.A.; Wert, E.C.; Rexing, D.J.; Zegers, R.; Drury, D.D. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone Sci. Eng.* **2006**, *28*, 445–460. [CrossRef]
18. Barber, L.B.; Keefe, S.H.; Kolpin, D.W.; Schnoebelen, D.J.; Flynn, J.L.; Brown, G.K.; Furlong, E.T.; Glassmeyer, S.T.; Gray, J.L.; Meyer, M.T.; et al. *Lagrangian Sampling of Wastewater Treatment Plant Effluent in Boulder Creek, Colorado, and Fourmile Creek, Iowa, during the Summer of 2003 and Spring of 2005—Hydrological and Chemical Data*; Open-File Report; U.S. Geological Survey: Reston, VA, USA, 2011; pp. 1054–1084.
19. Radjenovic, J.; Petrovic, M.; Barceló, D. Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. *Anal. Bioanal. Chem.* **2007**, *387*, 1365–1377. [CrossRef] [PubMed]
20. Yang, X.; Flowers, R.C.; Weinberg, H.S.; Singer, P.C. Ocurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. *Water Res.* **2011**, *45*, 5218–5228. [CrossRef] [PubMed]
21. Huber, M.M.; Korhone, S.; Ternes, T.A.; von Gunten, U. Oxidation of pharmaceuticals during water treatment with chlorine dioxide. *Water Res.* **2005**, *39*, 3607–3617. [CrossRef] [PubMed]
22. Lester, Y.; Avisar, D.; Gozlan, I.; Mamane, H. Removal of pharmaceuticals using combination of UV/H2O2/O3 advanced oxidation process. *Water Sci. Technol.* **2011**, *64*, 2230–2238. [CrossRef]
23. Solarchem Environmental Systems. Chemistry of advanced oxidation. In *The UV/Oxidation Handbook*; Solarchem Environmental Systems: Markham, ON, Canada; Las Vegas, NV, USA, 1994; Chapter 2; p. 13.
24. Epold, I.; Dulova, N.; Veressinina, V.; Trapido, M. Application of ozonation, UV photolysis, fenton treatment and other related processes for degradation of ibuprofen and sulfamethoxazole in different aqueous matrices. *J. Adv. Oxid. Technol.* **2012**, *15*, 354–364. [CrossRef]
25. Klavarioti, M.; Mantzavinos, D.; Kassinos, D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* **2009**, *35*, 402–417. [CrossRef]
26. Ternes, T.A.; Meisenheimer, M.; McDowell, D.; Sacher, F.; Brauch, H.J.; Gulden, B.H.; Preuss, G.; Wilme, U.; Seibert, N.Z. Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Technol.* **2002**, *36*, 3855–3863. [CrossRef]
27. Zwiener, C.; Frimmel, F.H. Oxidative treatment of pharmaceuticals in water. *Water Res.* **2000**, *34*, 1881–1885. [CrossRef]
28. Esplugas, S.; Bila, D.M.; Krause, L.G.T.; Dezotti, M. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *J. Hazard. Mater.* **2007**, *149*, 631–642. [CrossRef]
29. Garoma, T.; Umamaheshwar, S.K.; Mumper, A. Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. *Chemosphere* **2010**, *79*, 814–820. [CrossRef] [PubMed]
30. Paucar, N.E.; Kim, I.; Tanaka, H.; Sato, C. Ozone treatment process for the removal of pharmaceuticals and personal care products in wastewater. *Ozone Sci. Eng.* **2019**, *41*, 3–16. [CrossRef]
31. Park, J.; Yamashita, N.; Park, C.; Shimono, T.; Takeuchi, D.M.; Tanaka, H. Removal characteristics of pharmaceuticals and personal care products: Comparison between membrane bioreactor and various biological treatment processes. *Chemosphere* **2017**, *179*, 347–358. [CrossRef] [PubMed]
32. Hijnen, W.A.M.; Beerendonk, E.F.; Medema, G.J. Inactivation credit of UV radiation for viruses, bacteria and protozoan (00) Cysts in water: A review. *Water Res.* **2006**, *40*, 3–22. [CrossRef] [PubMed]
33. Parsons, S. *Advanced Oxidation Processes for Water and Wastewater Treatment*, 1st ed.; IWA Publishing: London, UK, 2004.
34. Chiou, C.H.; Wu, C.Y.; Juang, R.S. Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO_2 process. *Chem. Eng. J.* **2008**, *139*, 322–329. [CrossRef]
35. Hoigne, J.; Bader, H. Role of Hydroxyl radical reactions in ozonation processes in aqueous-solutions. *Water Res.* **1976**, *10*, 377–386. [CrossRef]

36. Peyton, G.R.; Glaze, W.H. Destruction of pollutants in water with ozone in combination with ultraviolet-radiation. 3. Photolysis of aqueous ozone. *Environ. Sci. Technol.* **1988**, *22*, 761–767. [CrossRef] [PubMed]
37. Poyatos, J.M.; Muñio, M.M.; Almecija, M.C.; Torres, J.C.; Hontoria, E.; Osorio, F. Advanced Oxidation Processes for Wastewater Treatment: State of the Art. *Water Air Soil Pollut.* **2010**, *205*, 187–204. [CrossRef]
38. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F.; Kerr, J.A.; Rossi, M.J.; Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement VI. IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1329–1499. [CrossRef]
39. Šojić, D.; Despotović, V.; Orčić, D.; Szabó, E.; Arany, E.; Armaković, S.; Illé, E.; Gajda-Schrantz, K.; Dombi, A.; Alapi, T.; et al. Degradation of thiamethoxam and metoprolol by UV, O3 and UV/O3 hybrid processes: Kinetics, degradation intermediates and toxicity. *J. Hydrol.* **2012**, *472*, 314–327. [CrossRef]
40. Staehelin, J.; Hoigné, J. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ. Sci. Technol.* **1985**, *19*, 1206–1213. [CrossRef]
41. Akmehmet, B.I.; Ötker, M. Pre-treatment of antibiotic formulation wastewater by O_3, O_3/H_2O_2 and O_3/UV processes. *Turk. J. Eng. Environ. Sci.* **2004**, *28*, 325–331.
42. Ku, Y.; Wang, W.; Shen, Y.S. Reaction Behaviors of Decomposition of Monocrotophos in Aqueous Solution by UV and UV/O_3 Processes. *J. Hazard. Mater.* **2000**, *72*, 25–37. [CrossRef]
43. Kallas, J.; Munter, R. Post treatment of pulp and paper industry wastewaters using oxidation and adsorption processes. *Water. Sci. Technol.* **1994**, *29*, 259–272. [CrossRef]
44. Singh, S. Ozone Treatment of Municipal Wastewater Effluent for Oxidation of Emerging Contaminants and Disinfection. Master's Thesis, University of Windsor, Windsor, ON, Canada, 2012.
45. Ministry of Land, Infrastructure, Transportation, and Tourism. *The Study on Endocrine Disruptors in Sewerage*; Ministry of Land, Infrastructure, Transportation, and Tourism: Tokyo, Japan, 2001.
46. Tainaka, T. The sewerage system in the Lake Biwa Basin. In Proceedings of the TAAL 2007: The 12th World Lake Conference, Jaipur, India, 28 October–2 November 2007; pp. 1417–1422.
47. Kim, I.H.; Yamashita, N.; Kato, Y.; Tanaka, H. Discussion on the application of UV/H_2O_2, O_3 and O_3/UV processes as technologies for sewage reuse considering the removal of pharmaceuticals and personal care products. *Water Sci. Technol.* **2009**, *59*, 945–955. [CrossRef]
48. Sato, C.; Kim, I.; Tanaka, H. Effect of H_2O_2 on UV photo-oxidation of pharmaceuticals and personal care products in wastewater. *J. Environ. Eng.* **2016**, *142*, 04016055. [CrossRef]
49. Bader, H.; Hoigne, J. Determination of ozone in water by the indigo method. *Water Res.* **1981**, *15*, 449–456. [CrossRef]
50. Ngoc, D.T.C.; Thi, K.Q.V.; Thanh, T.N.; Xuan, T.B. Performance of Ozonation process as advanced treatment for antibiotics removal in membrane permeate. *Geosci. Eng.* **2016**, *62*, 21–26.
51. Lee, C.O.; Howe, K.J.; Thomson, B.M. Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. *Water Res.* **2012**, *46*, 1005–1014. [CrossRef] [PubMed]
52. Schaar, H.; Clara, M.; Gans, O.; Kreuzinger, N. Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. *Environ. Pollut.* **2010**, *158*, 1399–1404. [CrossRef] [PubMed]
53. Dickenson, E.R.V.; Drewes, J.E.; Sedlak, D.L.; Wert, E.C.; Snyder, S.A. Applying surrogates and indicators to asses removal efficiency of trace organic chemicals during chemical oxidation of wastewaters. *Environ. Sci. Technol.* **2009**, *43*, 6242–6247. [CrossRef] [PubMed]
54. Giri, R.R.; Ozaki, H.; Ota, S.; Takanami, R.; Taniguchi, S. Degradation of common pharmaceuticals and personal care products in mixed solutions by advanced oxidation techniques. *Int. J. Environ. Sci. Technol.* **2010**, *7*, 251–260. [CrossRef]
55. Andreozzi, R.; Raffaele, M.; Nicklas, P. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere* **2003**, *50*, 1319–1330. [CrossRef]
56. Gagnon, C.; Lajeunesse, A.; Cejka, P.; Gagne, F.; Hausler, R. Degradation of selected acidic and neutral pharmaceutical products in a primary treated wastewater by disinfection processes. *Ozone Sic. Eng.* **2008**, *30*, 387–392. [CrossRef]
57. Reungoat, J.; Macova, M.; Escher, B.I.; Carswell, S.; Mueller, J.F.; Keller, J. Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. *Water Res.* **2010**, *44*, 625–637. [CrossRef]

58. Nakada, N.; Shinohara, H.; Murata, A.; Kiri, K.; Managaki, S.; Sato, N.; Takada, H. Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Res.* **2007**, *41*, 4373–4382. [CrossRef] [PubMed]
59. Deng, Y.; Zhao, R. Advanced Oxidation Processes (AOPs) in Wastewater treatment. *Curr. Pollut. Rep.* **2015**, *1*, 167–176. [CrossRef]
60. Ikehata, K.; Jodeiri Naghashkar, N.; Gamal El-Din, M. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. *Ozone Sci. Eng.* **2006**, *2*, 353–414. [CrossRef]