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Oxidative Treatments of Pesticides in Rainwater Runoff by HOCl, O₃, and O₃/H₂O₂: Effects of pH, Humic Acids and Inorganic Matters

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Abstract: This study systematically investigated the oxidative treatment of five selected pesticides, alachlor (ALA), carbendazim (CAR), diuron (DIU), pyrimethanil (PYR), and tebuconazole (TEB), by comparing their relative reactivities as a function of three different oxidative treatment processes (i.e., chlorine (HOCl), ozone (O₃), and ozone/hydrogen peroxide (O₃/H₂O₂)) under various oxidant dosages, reaction times, and pH conditions. For oxidative treatment, pesticide standards were spiked into rainwater. The removal efficiency of the selected pesticides varied considerably depending on the oxidative treatment processes. HOCl, O₃, and O₃/H₂O₂ treatments were highly effective at eliminating CAR (>80%) and PYR (>99%), while they were not significantly effective in removing TEB (<20%). In the case of DIU, HOCl (81%) was shown to be more effective than O₃ (24%) and O₃/H₂O₂ (49%). The removal efficiency of ALA was in the order of O₃/H₂O₂ (49%) > O₃ (20%) > HOCl (8.5%). The effect of increasing the solution pH from 5.0 to 9.0 on pesticide degradation varied between the oxidative treatment processes. Additionally, NH₄⁺, NO₂⁻, and humic acid in rainwater significantly inhibited pesticide degradation.

Keywords: chlorine; hydroxyl radical; ozone; pesticides; rainwater

1. Introduction

Pesticides are commonly used to enhance crop production and prevent plant diseases, such as fungal infections [1]. The United States Environmental Protection Agency reported that the global application of pesticides totaled more than 2 million tons and over USD 39 billion in 2007 [2]. Although most pesticide contamination occurs due to pesticide use in agricultural fields, the use of pesticides in urban areas has gained further attention owing to their potential risk to the environment and human health (e.g., mutagenicity, toxicity, and carcinogenicity) [3]. Several studies have demonstrated the presence of pesticides in urban rainwater globally [4,5]. Alachlor (ALA) and diuron (DIU) were detected in rainwater samples in Strasbourg, France, with maximum concentrations of 5590 and 1025 ng/L, respectively [4]. Tebuconazole (TEB) was detected in Brunswick Land (Germany) in concentrations ranging between 12 and 187 ng/L [5] (Supplementary information, Table S1).

Water shortage has become a significant global problem due to climate change, rapid population growth, and urbanization. There is an increasing demand for alternative water sources, such as rainwater, to secure a sustainable water supply [6]. In recent years, rainwater has attracted attention as an urban water resource for plant irrigation, flushing toilets, laundry, and cleaning [7,8]. However, a wide range of micropollutants, including pesticides, pharmaceuticals, and endocrine-disrupting chemicals, have been detected in...
significant quantities in rainwater runoff [9]. Several studies have demonstrated that various pesticides may be detected in rainwater due to the high pesticide variability [4,10]. Although the average concentration of pesticides detected in rainwater is low (µg/L), the potential toxicity of pesticides can increase the risk associated with rainwater reuse [11]. Furthermore, rainwater can trigger the transport of pollutants, including pesticides and particulate matter, into surface water [12]. Therefore, pesticides must be eliminated during the rainwater treatment process.

Conventional treatment technologies, such as physical and biological treatments, are designed to mitigate pesticides from rainwater [13]. However, several researchers have found that the performance of these treatment technologies is not sufficient to reduce pesticides due to their variability. Although chemical oxidation processes using chlorine (HOCl), ozone (O₃), and O₃ with hydrogen peroxide (O₃/H₂O₂) are relatively expensive compared to physical and biological treatments, these processes are more effective and stable for removing organic pollutants, including pesticides. Furthermore, these oxidation processes are more suitable to satisfy the acceptable pesticides concentrations in water quality regulations (U.S.EPA regulation for drinking water: ALA = 400 µg/L and DIU = 70 µg/L) to reuse rainwater for potable and irrigation waters [14]. The HOCl is the most commonly used oxidant in the water treatment process globally due to its low operating cost, high efficiency, and stability of chlorine residue in the distribution system, despite the disadvantage of producing harmful disinfection by-products, including trihalomethane (THM) and haloacetic acids (HAAs) [15]. O₃ has been proven to be effective for micropollutant degradation through direct reaction with molecular O₃ and indirect reaction with hydroxyl radicals produced by O₃ decomposition [16]. In recent years, water and wastewater treatment plants have applied the O₃/H₂O₂ advanced oxidation process (AOP) due to its relatively higher effectiveness compared to the corresponding conventional ozonation process [17]. However, there is a need for a comprehensive study on the effects of rainwater treatment via HOCl, O₃, and O₃/H₂O₂ on the removal behaviors of pesticides.

The primary purpose of this study was to provide valuable insights into the removal behavior of selected pesticides during the HOCl, O₃, and O₃/H₂O₂ processes. Therefore, the degradation of components in the rainwater by the oxidation process was identified and directly correlated to the decrease in the selected pesticides to evaluate the efficiency of HOCl, O₃, and O₃/H₂O₂. Furthermore, the effects of pH, humic acid (HA), and inorganic matters on the removal efficiency of the selected pesticides were systematically investigated to elucidate their degradation mechanisms in the three different oxidation processes.

2. Materials and Methods
2.1. Rainwater Sample Collection
Rainwater samples (n = 4) were collected within initial precipitation (within 4 h after rainfall) between July and September 2019 from the engineering building rooftop in Kang-won National University (Chunchen-si, Republic of Korea; latitude 37°52'05" N, longitude 127°44'19" E) using acid-cleaned funnels (45 cm diameter) connected to a polyethylene bottle. Chuncheon-si is located approximately 110 km to the east of Seoul (capital city), Republic of Korea. The rainwater samples were immediately filtered using cellulose nitrate membranes (Sartorius Stedim Biotech, Goettingen, Germany) with a pore size of 0.45 µm and stored in amber glass bottles (2 L) at 4°C.

2.2. Pesticides and Reagents
Five different pesticides, ALA (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide), carbendazim (CAR, methyl N-(1H-benzimidazol-2-yl) carbamate), DIU (1-(3,4-dichlorophenyl)-3,3-dimethyurea), pyrimethanil (PYR, 4,6-dimethyl-N-phenylpyrimidin-2-amine), and TEB (1-(4-chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl) pentan-3-ol), were selected as representative compounds with various functional groups closely related to HOCl, O₃, and O₃/H₂O₂ reactivities, and p-chlorobenzoic acid (pCBA) was used to probe these compounds for hydroxyl radicals (Table 1). Sodium hypochlorite
(NaOCl) containing 5% free chlorine was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan), and H₂O₂ (30 wt% solution) was purchased from Daejung Chemicals & Metals Co., Ltd. (Siheung-si, Republic of Korea). Sodium hydroxide (NaOH), hydrochloric acid (HCl), HA, ammonium acetate (>98%), sodium nitrite (>97%), and potassium phosphate monobasic (>99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). High-performance liquid chromatography (HPLC)-grade acetonitrile (ACN) was obtained from J.T. Baker (Deventer, The Netherlands), and phosphoric acid (H₃PO₄) was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Deionized (DI) water (resistivity >18.2 MΩ cm⁻¹) was used to prepare stock solutions of the selected pesticides (concentration of each pesticide = 1 mmol/L). These stocks were stored at 4 °C in the dark before use. The physicochemical properties of the selected pesticides are summarized in Table 1.

Table 1. Physicochemical characteristics of the selected pesticides.

| Compounds (Abbreviation) | Use     | Structure | Molecular Weight a (g/mol) | Solubility in Water a (g/L, pH 7) | UVA Detection (nm) | pKa a | Guideline for Drinking Water (μg/L) | Ref. |
|--------------------------|---------|-----------|---------------------------|----------------------------------|-------------------|-------|------------------------------------|------|
| Alachlor (ALA)           | Herbicide | ![Structure](image1) | 269.77                    | 0.03                             | 210               | -     | 20 (WHO) 400 (U.S. EPA)           | [14, 18] |
| Carbendazim (CAR)        | Fungicide | ![Structure](image2) | 191.19                    | 0.43                             | 210               | 4.28  | -                                  | [1]  |
| Diuron (DIU)             | Herbicide | ![Structure](image3) | 233.09                    | 0.18                             | 210               | 13.18 | 70 (U.S. EPA)                     | [14, 18] |
| Pyrimethanil (PYR)       | Fungicide | ![Structure](image4) | 199.25                    | 0.25                             | 210               | 3.44  | -                                  | [1]  |
| Tebuconazole (TEB)       | Fungicide | ![Structure](image5) | 307.82                    | 0.06                             | 210               | 2.01  | -                                  | [1]  |
| Para-Chlorobenzoic Acid (pCBA) | OH radical Probe compound | ![Structure](image6) | 156.57                    | 156.57                           | 240               | 4.07  | -                                  | [19] |

a ChemAxon (http://www.chemicalize.org (accessed on 2 February 2021)).

2.3. Experimental Procedures

Oxidant consumption experiments for HOCl and O₃ were conducted for rainwater, where each oxidant was applied at a dosage of 40 μM at pH 6.6 in 20 mL reaction volume. Samples (5 mL) were collected to measure residual oxidants at several time intervals: 0.5, 1, 2, 5, 10, and 30 min. HOCl, O₃, and O₃/H₂O₂ oxidation experiments were carried out on a bench-scale using rainwater at pH 6.6 and the range of specific O₃
values (0.17–0.20 mg/s; O₃ generator, LAB-II, Ozone Tech, Daejeon, Republic of Korea) and HOCl (oxidant/dissolved organic carbon (DOC) = 10, 20, 30, and 40 µM) and H₂O₂ (molar ratio = 0.5) dosages at room temperature (25 ± 1 °C) (Figure 1). Each pesticide was spiked into a 25 mL reaction bottle at a concentration of 2 µM. For the O₃/H₂O₂ experiment, a stock solution of H₂O₂ was added before adding the O₃. At the end of the reaction time (30 min), the samples were immediately quenched with 50 µL of thiosulfate solution (100 mM) and analyzed for residual pesticide concentrations using HPLC.

![Diagram](image.png)

Figure 1. The diagram for batch-scale oxidation experiments for pesticides in rainwater samples.

2.4. Analytical Methods

The concentrations of the selected pesticides (i.e., ALA, CAR, DIU, PYR, and TEB) in the rainwater samples were quantified using high-performance liquid chromatography (HPLC) fitted with an ultraviolet absorbance (UVA) detector (SPD-10AVP, Shimadzu, Kyoto, Japan) and an XDB C18 column (ZORBAX Eclipse ®, 4.6 × 150 mm, inner diameter = 5 µm, Agilent, Santa Clara, CA, USA) at a constant flow rate of 1.0 mL/min for 15 min. Acetonitrile/0.05 M phosphoric acid (50:50, v/v) at a 1.0 mL/min flow rate was used as the mobile phase for ALA, CAR, DIU, PYR, TEB, and pCBA. The wavelength of the UVA detector was set at 210 nm for the selected pesticides and 240 nm for p-CBA. A total organic carbon analyzer (TOC-V CPH, Shimadzu, Kyoto, Japan) equipped with total dissolved nitrogen (TN) measuring unit (TNM-1, Shimadzu, Kyoto, Japan) was used to quantify the DOC and TN in rainwater (detection limits for DOC and TN were 0.012 mg C/L and 0.006 mg N/L, respectively). Inorganic ions, such as ammonia (NH₄⁺), sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺), chlorine (Cl⁻), nitrite (NO₂⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻), and phosphate (PO₄³⁻), were measured using ion chromatography (761 Compact IC, Metrohm, Herisau, Switzerland). NH₄⁺ and NO₂⁻ ions were determined by colorimetric methods at 655 (DIN 38 406, German standard methods) and 540 nm (DIN EN 26 777, German standard methods), respectively. Several colorimetric methods have been used to measure the oxidant concentrations in rainwater. The dissolved O₃ in the rainwater samples were detected using the indigo method (UV wavelength = 600 nm, Ozone Accuvac ® Amplules, Hach Company, Loveland, CO, USA), and the determination of free chlorine quantification was used by the N,N-diethyl-p-phenylenediamine (DPD) free chlorine kit and colorimeter (Hach Company, Loveland, CO, USA) [19,20].

2.5. Statistical Analysis

The statistical analysis was carried out using a SigmaPlot (Version 12.5, Systat Software, Inc, CA, USA). All experiments were performed in triplicate. Furthermore, the results (i.e., mean ± standard deviation) are presented in the manuscript.

3. Results and Discussion

3.1. Rainwater Quality Analyses

Table 2 shows the physicochemical characteristics of the rainwater samples at the study site. The conductivity and pH values were not significantly different during collecting periods (conductivity: 1.9–2.0 µS/cm; pH: 6.5–6.6). The average conductivity value (2.0 µS/cm) of the rainwater was considerably lower than that of the Korean urban precipitation (Goyang = 13.9 mS/cm; Gangneung = 30 µS/cm). In contrast, the mean pH value of 6.6 was slightly higher than that of other urban areas (Goyang = 5.6; Gangneung = 5.3) [21,22]. Moreover, the rainwater has fewer inhibition factors for oxidation treatments due to low DOC (0.4 mgC/L) and inorganic nitrogen species (TN = 70.2 µgN/L, NO₃⁻ = 51.3 µgN/L).
Na⁺ and Ca²⁺ were the most abundant cations, and Cl⁻ and SO₄²⁻ were the most abundant anions. Other rainwater contents, such as NO₃⁻, NH₄⁺, and Mg²⁺, were found in µg/L levels.

Table 2. Rainwater quality parameters (n = 3).

| Parameters                 | Conditions          |
|----------------------------|---------------------|
| pH                        | 6.6 ± 0.05          |
| Conductivity (µS/cm)      | 2.0 ± 0.03          |
| DOC (µgC/L)               | 375 ± 1.5           |
| TN (µgN/L)                | 70.2 ± 2.0          |
| NO₂⁻ (µgN/L)              | N.D.                |
| NO₃⁻ (µgN/L)              | 51.3 ± 2.2          |
| Cl⁻ (µg/L)                | 198 ± 1.9           |
| SO₄²⁻ (µg/L)              | 485 ± 3.2           |
| PO₄³⁻ (µg/L)              | N.D.                |
| NH₄⁺ (µgN/L)              | 18.6 ± 1.7          |
| Na⁺ (µg/L)                | 274 ± 7.8           |
| Ca²⁺ (µg/L)               | 206 ± 4.5           |
| Mg²⁺ (µg/L)               | 48.8 ± 8.0          |

N.D. = Not detected.

3.2. Consumption Kinetics of HOCl and O₃ in Rainwater Sample

Figure 2 presents the HOCl and O₃ consumption kinetics in a rainwater sample at pH 6.6 for each oxidant dose of 40 µM. The rainwater sample had a low concentration of inorganic nitrogen species, such as NO₃⁻ = 0.83 µM (51.3 µg N/L) and NH₄⁺ = 1.03 µM (18.6 µg N/L). Therefore, the consumption of HOCl and O₃ was predominantly affected by DOC (0.4 mgC/L (13.2 µM)). HOCl showed rapid consumption (29%) within 2 min from the initial oxidant dose (in terms of the initial phase), followed by a slow decrease over the next 60 min of reaction time (in terms of the second phase, the consumption rate = 70%). In contrast, O₃ depleted in less than 30 min (the consumption rate during the initial phases = 49%). Similar decay behaviors have been observed in the removal of effluent organic matter in secondary wastewater effluent by HOCl and O₃ [23].

3.3. Effects of Oxidant Dosages

The removal efficiencies of the selected pesticides were compared in the rainwater samples using selective (HOCl and O₃) and non-selective (hydroxyl radicals: O₃/H₂O₂)
oxidants. With increasing oxidant dosage, the degradation of the selected pesticide’s removal efficiency increased. Figure 3 shows that the removal efficiencies of CAR, PYR, and DIU by HOCl and O₃ were between 15% and 50% for 10 μM oxidant concentration after 30 min, while the removal efficiency of ALA and TEB was only 9.5% under the same experimental conditions. After increasing the oxidant concentration to 40 μM, the removal efficiency of CAR and DIU reached between 40% and 90% after 30 min, while the efficiency of ALA and TEB was enhanced to 21%. PYR was fully degraded with all oxidants. For HOCl and O₃ (the selective oxidants), there was a lag phase at lower oxidant dosages, where the pesticide concentration decreased slightly with increasing oxidant dosage (Figure 2a,b). The low removal efficiency in the lag phase was attributed to the high competition for the selective oxidants between the CAR and PYR and the DOC [23]. Additionally, with an increase in the selective oxidant dosages higher than the initial consumption by DOC, the residual concentrations of CAR and PYR started to decrease significantly. However, the removal rates of ALA and TEB were less than 21% for HOCl and O₃ processes. In contrast, in the case of O₃/H₂O₂, the removal efficiencies of the selected pesticides were linearly proportional to the applied hydroxyl radical dosage (Figure 3c). These observations indicate that the magnitude of the competition for hydroxyl radicals between pesticides and rainwater matrix remained constant during the entire oxidation process. Based on these experiments on the removal efficiency of the selected pesticides according to the HOCl, O₃, and O₃/H₂O₂ dosages, 40 μM was selected as the optimal dosage and used in subsequent experiments.

![Figure 3](image-url)

**Figure 3.** The effects of the oxidant dosage on the removal efficiencies of the selected pesticides by (a) HOCl, (b) O₃ and (c) O₃/H₂O₂ (initial concentration of each pesticide and pCBA = 2 μM, reaction time = 0.5 h, temperature = 25 °C, pH = 6.6).

### 3.4. Removal Efficiency of the Selected Pesticides in Rainwater Samples by HOCl, O₃ and O₃/H₂O₂

Figure 4 presents the removal efficiencies of the selected pesticides in the rainwater sample during the HOCl, O₃, and O₃/H₂O₂ processes at pH 6.6 for 0.5 h (each oxidant dose of 40 μM). For ALA and TEB, the removal efficiencies of HOCl, O₃, and O₃/H₂O₂ were in the order of O₃/H₂O₂ (ALA = 49% and TEB = 23%) > O₃ (ALA = 20% and TEB = 17%) > HOCl (ALA = 9% and TEB = 13%) (Figure 4a, e). ALA was reported to be lowly reactive with HOCl due to the inhibitive effect of the acetanilide functional group in the ALA. In addition, the ethyl groups of the ortho positions in the aromatic ring on the ALA reduced the reactivity toward the electrophilic attack of O₃ to the aromatic moieties [24]. The relatively higher reactivity of TEB with O₃/H₂O₂ compared with HOCl and O₃ might be caused by the reaction between the aromatic C₆-cycle or the C₅ aromatic N-heterocycle and hydroxyl radicals [25]. The removal efficiencies of CAR, DIU, and PYR by HOCl (CAR = 98%, DIU = 92% and PYR = 100%) were more efficient than those of O₃ (CAR = 81%, DIU = 49%, and PYR = 99%) and O₃/H₂O₂ (CAR = 92%, DIU = 24%, and PYR = 98%) (Figure 4b–d). CAR and PYR were highly reactive to HOCl and O₃, and O₃/H₂O₂ due to the reaction sites of the CAR (C=O double bond) and PYR (the nitrogen bridge between the...
two rings, the phenyl ring, and the pyrimidyl ring) \cite{26,27}. DIU was lowly reactive with O3 due to the nitrogens at the urea function groups and the aromatic ring with the two chlorine atoms \cite{28}. These findings suggest that choosing an appropriate oxidation process is important as the reactivity of the oxidant varies with the type of pesticide.

![Graphs showing removal efficiencies of ALA, CAR, DIU, PYR and TEB](image)

Figure 4. Removal efficiencies of (a) ALA, (b) CAR, (c) DIU, (d) PYR and (e) TEB by HOCl, O3, and O3/H2O2 in the rainwater (initial concentration of each pesticide = 2 μM, reaction time = 0.5 h, temperature = 25 °C, pH = 6.6).

3.5. Effects of pH on the Removal of the Selected Pesticides

The changes in removal efficiencies of the selected pesticides during the HOCl, O3, and O3/H2O2 processes as a function of the pH of the rainwater samples are presented in Table 3. In general, the reactivities of the selected pesticides with HOCl, O3, and O3/H2O2 increased as the pH increased. However, in CAR, DIU, and PYR, their removal efficiencies in the chlorinated rainwater samples were strongly dependent on the pH condition. These results could be attributed to the accelerated reaction of HOCl in the chlorinated rainwater at pH 7, which was closely related to the removal of CAR, DIU and PYR \cite{29}. 

![Graphs showing removal efficiencies of ALA, CAR, DIU, PYR and TEB](image)
Table 3. The effects of pH on the removal efficiencies (%) of the selected pesticides by HOCl, O$_3$ and O$_3$/H$_2$O$_2$ processes (initial concentration of each pesticide = 2 µM, reaction time = 0.5 h, temperature = 25 °C).

|          | HOCl pH 5 | pH 7 | pH 9 | O$_3$ pH 5 | pH 7 | pH 9 | O$_3$/H$_2$O$_2$ pH 5 | pH 7 | pH 9 |
|----------|-----------|------|------|-----------|------|------|----------------------|------|------|
| ALA      | 8.8 ± 0.3 | 10.4 ± 0.2 | 13.5 ± 0.2 | 18.8 ± 0.2 | 19.7 ± 0.1 | 20.6 ± 0.3 | 48.6 ± 0.01 | 49.6 ± 0.03 | 49.9 ± 0.01 |
| CAR      | 97.8 ± 1.0 | 99.0 ± 0.01 | 77.6 ± 0.9 | 72.7 ± 1.2 | 91.7 ± 1.8 | 93.0 ± 2.0 | 66.4 ± 2.2 | 79.4 ± 2.1 | 80.5 ± 1.4 |
| DIU      | 68.6 ± 1.2 | 80.0 ± 1.2 | 78.6 ± 0.9 | 19.5 ± 1.0 | 240 ± 1.4 | 32.1 ± 1.3 | 426.4 ± 1.4 | 495.1 ± 1.2 | 53.0 ± 0.2 |
| PYR      | 99.5 ± 0.5 | 99.9 ± 0.2 | 60.7 ± 0.9 | 64.2 ± 1.9 | 99.0 ± 0.1 | 99.1 ± 0.2 | 90.9 ± 1.6 | 99.0 ± 0.2 | 99.5 ± 0.4 |
| TEB      | 4.0 ± 0.1 | 13.2 ± 0.2 | 24.4 ± 0.2 | 14.4 ± 0.3 | 17.4 ± 0.2 | 25.5 ± 1.2 | 17.0 ± 1.0 | 22.7 ± 1.4 | 30.3 ± 2.0 |

3.6. Effects of Humic Acids on the Removal of the Selected Pesticides

The consumption of oxidants by HA is a significant factor in determining the removal efficiency of the selected pesticides. In the presence of HA (Table 4), a significant abatement in the removal efficiency (reaction time = 0.5 h) of the selected pesticides was found for the HOCl processes. Despite the higher removal efficiency of CAR, DIU, and PYR during the HOCl, O$_3$, and O$_3$/H$_2$O$_2$ processes compared to other pesticides, the influence of HA on the decrease in the selected pesticides was more pronounced in the O$_3$/H$_2$O$_2$ treated rainwater samples (the difference between the relative residual concentrations (Δ/C/C$_0$) of CAR, DIU, and PYR without and with 4 mg/L HA = 0.96, 0.75 and 0.41, respectively) than that for the chlorinated rainwater samples (Δ/C/C$_0$ of CAR, DIU, and PYR without and with 4 mg/L HA = 0.31, 0.42 and 0.018, respectively) due to the phenolic group in HA, which could easily react with dissolved O$_3$ and hydroxyl radicals during the O$_3$/H$_2$O$_2$ processes [23]. Similar behaviors were observed for removal efficiencies of micropollutants by microbubble ozone in the HA presence condition [19].

Table 4. The effects of HA on the removal efficiencies (%) of the selected pesticides by HOCl, O$_3$ and O$_3$/H$_2$O$_2$ processes (initial concentration of each pesticide = 2 µM, the concentrations of HA = 0, 1, and 4 mg/L, reaction time = 0.5 h, temperature = 25 °C).

|          | HOCl HA 0 | HA 1 | HA 4 | O$_3$ HA 0 | HA 1 | HA 4 | O$_3$/H$_2$O$_2$ HA 0 | HA 1 | HA 4 |
|----------|-----------|------|------|-----------|------|------|----------------------|------|------|
| ALA      | 95 ± 0.1  | 8.5 ± 0.2 | 5.3 ± 0.2 | 19.1 ± 1.0 | 14.5 ± 0.9 | 12.2 ± 1.0 | 49.0 ± 1.2 | 46.8 ± 0.9 | 34.4 ± 1.6 |
| CAR      | 98.2 ± 1.0 | 97.8 ± 1.3 | 67.9 ± 0.9 | 91.7 ± 1.1 | 60.7 ± 1.0 | 10.6 ± 1.2 | 80.7 ± 0.8 | 35.1 ± 1.0 | 3.2 ± 0.1 |
| DIU      | 79.2 ± 1.2 | 68.5 ± 1.0 | 45.9 ± 1.0 | 23.8 ± 0.9 | 20.0 ± 1.0 | 16.7 ± 1.1 | 49.5 ± 1.3 | 19.0 ± 0.9 | 12.1 ± 0.6 |
| PYR      | 99.9 ± 0.2 | 99.5 ± 0.1 | 98.1 ± 0.3 | 99.0 ± 0.1 | 98.0 ± 0.8 | 95.3 ± 0.2 | 99.4 ± 0.3 | 74.1 ± 1.2 | 58.9 ± 0.4 |
| TEB      | 13.2 ± 1.0 | 9.3 ± 0.6 | 3.7 ± 0.5 | 17.4 ± 1.1 | 12.0 ± 0.9 | 9.6 ± 0.7 | 22.7 ± 1.2 | 15.7 ± 1.0 | 13.6 ± 1.0 |

3.7. Effects of Inorganic Matters on the Removal of the Selected Pesticides

Inorganic matters, including NO$_2^-$ and NH$_4^+$, generally exist in surface water and can rapidly consume the selective and non-selective oxidants and affect the removal efficiency of the selected pesticides. The rainwater samples spiked (4 mg/L) with additional NO$_2^-$ and NH$_4^+$ was treated with the predetermined oxidant dosage. Figure 5 shows that, in the case of HOCl and O$_3$/H$_2$O$_2$, NH$_4^+$ considerably decreased the removal efficiencies of ALA, CAR, DIU, PYR, and TEB. Remarkably, the DIU removal efficiency decreased by more than 55% for the HOCl-treated rainwater samples in the presence of NH$_4^+$ as HOCl rapidly reacted with NH$_4^+$ [30]. NH$_4^+$ significantly reduced the removal efficiencies of CAR and PYR during the O$_3$/H$_2$O$_2$ treatment process (C/C$_0$ of CAR without NH$_4^+$: 0.19; C/C$_0$ of CAR with NH$_4^+$: 0.81; C/C$_0$ of PYR without NH$_4^+$: 0.004; C/C$_0$ of PYR with NH$_4^+$: 0.46). In the case of O$_3$, the interference effects on selected pesticides were affected by NO$_2^-$, which was consistent with the relatively high k-value (3.7 × 10$^3$ M$^{-1}$ S$^{-1}$) of O$_3$ with NO$_2^-$ (C/C$_0$ without NO$_2^-$: ALA = 0.80, CAR = 0.083, DIU = 0.65, PYR = 0.001, TEB = 0.82; C/C$_0$ with NO$_2^-$: ALA = 0.86, CAR = 0.55, DIU = 0.88, PYR = 0.060, TEB = 0.94) [31]. Therefore,
these observations suggest that suitable pretreatment processes are needed to enhance the removal efficiency of the selected pesticides in rainwater during the oxidation process.

4. Conclusions

In this study, the potential of the various oxidant processes for the abatement of selected pesticides was evaluated and compared to the HOCl, O₃ (i.e., the selective oxidants), and O₃/H₂O₂ (i.e., hydroxyl radical as the non-selective oxidant) processes to provide deeper insights into the removal behavior of the selected pesticides. The primary outcomes were as follows:

- DOC is a major rainwater component and has a more significant influence on the consumption kinetics of the oxidants in rainwater than inorganic nitrogen species;

Figure 5. The effects of inorganic matter on the removal efficiencies of (a) ALA, (b) CAR, (c) DIU, (d) PYR and (e) TEB by HOCl, O₃, and O₃/H₂O₂ (initial concentration of each pesticide = 2 μM, the concentration of each inorganic matter = 4 mg/L, reaction time = 0.5 h, temperature = 25 °C, pH = 6.6).
• The dosage of oxidants for the removal of 90% CAR was in the order of HOCl (18 µM) > O₃ (21 µM) > O₃/H₂O₂ (25 µM), and the dosage of oxidants for removal of 90% PYR was in the order of O₃/H₂O₂ (9 µM) > O₃ (11 µM) > HOCl (20 µM);

• The removal efficiencies of CAR, DIU, and PYR by HOCl were more efficient than those of O₃ and O₃/H₂O₂. In contrast, O₃/H₂O₂ was the most effective oxidant for removing ALA and TEB;

• In general, the reactivities of the selected pesticides toward the HOCl, O₃, and O₃/H₂O₂ increased due to deprotonation when the pH of the rainwater sample was higher than the pKa values of the selected pesticides;

• The interference effects of HA and inorganic matter in the rainwater on removing the selected pesticides were more significant during the O₃/H₂O₂ process than those of the other oxidation processes;

• These findings suggest that the oxidation processes (i.e., HOCl, O₃, and O₃/H₂O₂) might be a promising method to enhance the removal efficiencies of organic pollutants, including pesticides, practically applicable for the wastewater treatment process.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/separations8070101/s1, Table S1: Concentrations of pesticides in rainwater.

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Abbreviations

- ALA: Alachlor
- C: Concentration of the selected pesticide after oxidation (µmol/L)
- C₀: Initial concentration of the selected pesticide (µmol/L)
- CAR: Carbendazim
- DIU: Diuron
- DOC: Dissolved organic carbon
- HA: Humic acids
- HOCl: Chlorine
- NO₂⁻: Nitrite
- NH₄⁺: Ammonia
- O₃: Ozone
- O₃/H₂O₂: Ozone/hydrogen peroxide
- pCBA: p-chlorobenzoic acid
- PYR: Pyrimethanil
- TEB: Tebuconazole
- TN: Total nitrogen

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