Abstract: Plastic products in municipal solid waste result in the extraction of phthalates in leachate that also contains large amounts of organic matter, such as humic substances, ammonia, metals, chlorinated organics, phenolic compounds, and pesticide residues. Phthalate esters are endocrine disruptors, categorized as a priority pollutant by the US Environmental Protection Agency (USEPA). Biological processes are inefficient at degrading phthalates due to their stability and toxic characteristics. In this study, the peroxone (ozone/hydrogen peroxide) process \( \text{O}_3/\text{H}_2\text{O}_2 \), an \( \text{O}_3 \)-based advanced oxidation process (AOP), was demonstrated for the removal of diethyl phthalate (DEP) in synthetic leachate simulating solid-waste leachate from an open dump. The impact of the \( \text{O}_3 \) dose during DEP degradation; the formation of ozonation intermediate by-products; and the effects of \( \text{H}_2\text{O}_2 \) dose, pH, and ultraviolet absorbance at 254 nm (UVC) were determined during ozonation. Removal of 99.9% of an initial 20 mg/L DEP was obtained via 120 min of ozonation (transferred \( \text{O}_3 \) dose \( = 4971 \text{ mg/L} \)) with 40 mg/L \( \text{H}_2\text{O}_2 \) in a semi-batch \( \text{O}_3 \) system. Degradation mechanisms of DEP along with its intermediate products were also determined for the AOP treatment. Indirect OH radical exposure was determined by using a radical probe compound (pCBA) in the \( \text{O}_3 \) treatment.

Keywords: advanced oxidation; diethyl phthalate (DEP); leachate; peroxone; solid waste; plastic; landfill

1. Introduction

Rapid urbanization and rising living standards have a major influence on the quantity and characteristics of municipal solid waste (MSW), further complicating the management and maintenance of sanitary landfills. Leachate is generated by the interaction of MSW with water that percolates through the landfill, producing highly polluted wastewater [1]. Many factors govern the quality and quantity of leachate, such as the composition of the waste, piling, seasonal variation, landfill technique, and structure of the landfill. In developed countries, possible options for leachate treatment include co-treatment with municipal wastewater and transportation to an ex situ treatment facility; however, even these treatment processes are not practiced nor affordable. Other advanced techniques include reverse osmosis and recirculation of the concentrated leachate back to the landfill to avoid groundwater contamination [2]. In many developing countries, open dumpsites serve as a final
disposal point for the MSW; these are a burden for the environment as the leachate is not collected or treated. One of the major concerns in the generation of leachate, in terms of both quantity and quality, is groundwater contamination [1]. Leachate extracts multiple contaminants from MSW and creates complex interactions between hydrological and biogeochemical reactions. Leachate contains a large amount of organic matter consisting of humic substances, along with ammonia nitrogen, heavy metals, chlorinated organics, and phenolic compounds.

Phthalate esters, known as phthalates, are plasticizers that are used to increase the quality and durability of polymers [3]. Phthalates leach and migrate from the plastic products into the environment as they are bonded to the products by physical and not chemical means, posing serious environmental and human health problems [4]. Phthalates, considered priority pollutants, have broad applications worldwide; they have a high biological toxicity to humans and are considered endocrine disruptor compounds (EDC) by the US Environmental Protection Agency (USEPA), European Environmental Agency (EEA), and other environmental agencies [5]. Specifically, diethyl phthalate (DEP) is commonly found in leachate and groundwater due to its high solubility and wide use in many items, among them being cosmetics, paints, and toys [5]. The USEPA-issued national primary drinking water regulation regarding organic chemical contaminants for DEP is 0.006 mg/L, which is the maximum permissible limit.

Studies have demonstrated the removal of organic contaminants and heavy metals from landfill leachate by various technologies, including pre-treatment techniques, such as a coagulation–flocculation process, stripping, and precipitation methods [6], followed by discharge to the municipal wastewater treatment plant, adsorption, or oxidation. Advanced oxidation processes (AOPs) have been successfully implemented for the degradation of recalcitrant substances from stabilized leachate (i.e., old leachate, which is less biodegradable) and to improve its biodegradation by increasing the ratio of biochemical to chemical oxygen demand (BOD$_5$/COD) [7].

Ozone (O$_3$) alone and in combination with different processes has been shown to efficiently degrade bulk organic contaminants from wastewater [8]. Organic compounds in leachate can be oxidized by either a direct reaction with O$_3$, or by O$_3$ decomposition to form the non-selective hydroxyl (OH) radicals at an alkaline pH; alternative methods include the addition of an oxidant such as hydrogen peroxide (H$_2$O$_2$) (termed peroxone process) or the addition of a catalyst at the natural water pH (7–8) [9]. For example, Amr et al. studied the removal of COD and color from a municipal landfill leachate using O$_3$ combined with a zinc sulfate oxidation process and obtained 90% and 99% removal for COD and color, respectively, with a 1 g/6 g ZnSO$_4$ dosage (COD$_0$/Zn) at 180 min of treatment time [10]. In addition, Amr et al. compared and optimized COD and color removal for a stabilized landfill leachate using three different AOP systems: O$_3$ alone, O$_3$/fenton, and O$_3$/persulfate [11]. The latter showed an improved performance efficiency compared to the other treatment processes for the removal of color, ammonia, and COD. Asaithambi et al. showed that the synergistic effect of a O$_3$/sonication/fenton-based AOP was more effective in treating leachate with minimal electrical energy for high removal efficiency of 100% color and 95% COD [4]. Several studies have shown the removal of DEP in water (not in leachate) using an AOP for the generation of OH radicals, such as ultraviolet radiation (UV)/TiO$_2$ [12], O$_3$ [13] and UV/H$_2$O$_2$ [5]. These studies demonstrated that OH radicals play a dominant role in AOP efficacy for DEP removal in water.

Due to the high percentage of plastics in MSW composition, there is a high concentration of phthalates in the leachate. However, the removal of phthalates by O$_3$-based AOP from the complex matrix of MSW leachate has never been explored. In this study, an O$_3$-based AOP—the peroxone process (O$_3$/H$_2$O$_2$)—was tested for the removal of DEP in a synthetic leachate simulating an MSW leachate from an open dump. The specific goal of this study was to demonstrate the impact of O$_3$ and H$_2$O$_2$ dose during degradation on DEP removal from the leachate and the formation of ozonation intermediate by-products, in addition to changes in COD, pH, and UVC during the process.
2. Materials and Methods

2.1. Chemical Reagents and Leachate Analysis

Leachate was prepared using DEP (>98%), phthalic acid (>98%), phthalic anhydride (>99%), 4-hydroxy phthalic acid (>98%) (Sigma Aldrich, USA), potassium hydrogen phthalate (KHP), glucose (C₆H₁₂O₆), ammonium sulfate (NH₄₂SO₄), ammonium chloride (NH₄Cl), copper sulfate (CuSO₄), lead nitrate (Pb(NO₃)₂), nickel sulfate (NiSO₄), potassium dichromate (K₂Cr₂O₇), manganese sulfate (MnSO₄), zinc sulfate (ZnSO₄), propionic acid (C₃H₆O₂), pentanoic acid (C₅H₁₀O₂), and hexanoic acid (C₆H₁₂O₂) (Holland Moran, Israel). Analytical grade H₂O₂ (30% w/w) was obtained from Merck Chemicals (USA). Stock solutions were prepared by dissolving each compound in deionized water (Direct-Q3 UV System, Millipore, France). COD test kits with a measuring range of 0 to 15,000 mg/L O₂ were purchased from Lavibond (England), and were based on the dichromate method and determination in a Hach spectrophotometer. The UV absorbance coefficients of the samples with different H₂O₂ concentrations were measured using a UV-visible spectrophotometer (Varian, Cary 100BIO, Australia). Spectra were collected in quartz cuvettes using a wavelength range of 200–800 nm.

2.2. Synthetic Leachate Preparation

The composition of the synthetic leachate was adapted from a previous study [14] and modified based on analyzed leachate samples from the Perungudi open dumpsite, Chennai, India, and previous data in the literature [15] (Table 1). The leachate characteristics used in this study simulated numerous samples of municipal solid waste, open dumpsite leachate from Chennai, India. In this leachate, diethyl phthalate (DEP) was detected at an average concentration of 17.2 mg/L in the open dumpsite. The leachate used in this study simulates young leachate.

| Parameter                  | Model Compound | Measured Value |
|----------------------------|----------------|----------------|
| pH                         | -              | 7.5            |
| Chemical oxygen demand     | KHP            | 16,400 mg/L    |
| Phthalate                  | Diethyl phthalate | 20 mg/L       |
| Chloride                   | NH₄Cl          | 1500 mg/L      |
| Manganese                  | MnSO₄          | 16 mg/L        |
| Zinc                       | ZnSO₄          | 12 mg/L        |
| Lead                       | Pb(NO₃)₂       | 2 mg/L         |
| Chromium                   | K₂Cr₂O₇       | 1.5 mg/L       |
| Copper                     | CuSO₄          | 2.5 mg/L       |
| Nickel                     | NiSO₄          | 4.5 mg/L       |
| Acetic acid                | Organic acid   | 7 mg/L         |
| Propionic acid             | Organic acid   | 5 mg/L         |
| Pentanoic acid             | Organic acid   | 1 mg/L         |
| Hexanoic acid              | Organic acid   | 1 mg/L         |

2.3. Experimental Setup and Procedure

O₃ experiments were performed in semi-continuous batch reactors that allowed for the continuous addition of O₃ to a fixed batch of leachate with added DEP, as shown in Figure 1. O₃ gas was generated using an O₂-fed O₃ generator (up to 4 g/h; BMT 802N, Germany) and the O₂–O₃ gas mixture was bubbled directly into a 100-mL glass reactor (Figure 1). The reactor was 14 cm in height and 3.5 cm in diameter, with a diffuser size of 2.35 cm² and a nominal pore size of 25 µm, as described in a previous study [16]. An O₃-flow control valve was used to determine the O₃ flow, which was maintained at 0.2 L/min operated under ambient conditions.
were COD, UVC, and pH. The impact of OH radicals on DEP-degradation kinetics using direct ozonation was determined in the presence of the radical scavenger tert-butanol (t-BuOH) (50, 100, 150, 200 mM). The radical probe compound para-chlorobenzoic acid (pCBA) was used at concentrations of 10 mg/L and 20 mg/L to determine the steady-state OH radical concentration for the degradation of DEP.

High-Performance Liquid Chromatography (HPLC) Analysis

An Agilent 1100 series HPLC system with single-wavelength UV detector was used for the analysis of both DEP and pCBA. The column was a Kinetex C18-XB column, 100 x 3.0 mm, 2.6 µm at 40 °C, with a Gemini C18 4 x 2.0 mm pre-column guard. The pump was set to an isocratic program of

\[
\text{Transferred Ozone Dose} \left( \frac{\text{mgO}_3}{L} \right) = \sum \left( C_{O_3,\text{in}} - C_{O_3,\text{out}} \right) \frac{\text{mg/L}}{\text{gas flowrate} \frac{L}{\text{min}}} \times \frac{\text{volume}_L}{\text{min}}
\]

where \( C_{O_3,\text{in}} \) is the \( O_3 \) concentration in the inlet stream, \( C_{O_3,\text{out}} \) is the \( O_3 \) concentration in the outlet stream, representing the unreacted \( O_3 \) exiting the reactor, and \( dt \) is the time interval between measurements, set at 1 min.

DEP (20 mg/L) was spiked into the synthetic leachate with the addition of 0, 5, 10, 20, 30, 40, and 50 mg/L of \( H_2O_2 \) to study the impact of \( H_2O_2 \) on DEP degradation along with the generated intermediate transformation products. The parameters recorded with the \( O_3 \) and \( O_3/H_2O_2 \) processes were COD, UVC, and pH. The impact of OH radicals on DEP-degradation kinetics using direct ozonation was determined in the presence of the radical scavenger tert-butanol (t-BuOH) (50, 100, 150, 200 mM). The radical probe compound para-chlorobenzoic acid (pCBA) was used at concentrations of 10 mg/L and 20 mg/L to determine the steady-state OH radical concentration for the degradation of DEP.

Figure 1. Semi-batch \( O_3 \) system experimental setup: (1) \( O_2 \) gas and flow-rate gauge; (2) air drier and humidity indicator; (3) \( O_3 \) generator; (4) gas inlet gauge; (5) air drier for \( O_3 \)-saturated air; (6,7) gas inlet and outlet, respectively; (8) \( O_3 \) diffuser; (9) solution inlet; (10) magnetic stir bar; and (11) sampling port.
40% water, 60% MeOH, and 0.1% formic acid (v/v), at a flow rate of 0.5 mL/min. The injection volume was 30 µL and the detector wavelength was set to 228 nm for DEP (retention time 3.0 min) and 243 nm for pCBA (retention time 2.5 min).

2.5. LC-MS Analysis

LC-MS analysis of the DEP degradation products phthalic acid and p-hydroxy phthalic acid (obtained after sample treatment with O$_3$/H$_2$O$_2$) was performed using HPLC (Agilent 1100) coupled to MS (Q-Tof, Waters, model Premier) via an electrospray ionization (ESI) interface in positive mode, using the Kinetex C18-XB column. The column temperature was set to 40 °C, the flow rate to 0.5 mL/min, and the injection volume was 30 µL. The HPLC mobile phase consisted of water (A) and methanol (B) with 0.1% formic acid. The elution gradient was initiated with 20% B, held for 2 min, increased to 65% over 11 min, and then held at 65% for 5 min.

3. Results and Discussion

3.1. DEP Removal in O$_3$ and O$_3$/H$_2$O$_2$ Processes

Synthetic leachate was spiked with 0.5 M (20 mg/L) DEP at pH 7.5 with various H$_2$O$_2$ concentrations (0, 5, 10, 20, 30, 40, and 50 mg/L) and ozonated to determine the ozonation kinetics. Figure 2 shows the degradation of DEP with the O$_3$ and O$_3$/H$_2$O$_2$ processes. The DEP concentration decreased by 21% with 120 min of ozonation only (TOD = 4971 mg/L). To increase the rate of DEP degradation, H$_2$O$_2$ was added to accelerate the production of OH radicals for the efficient degradation of DEP from leachate using the peroxone process.

![Figure 2. Diethyl phthalate (DEP) removal with peroxone process.](image-url)

The degradation rate of DEP increased with increasing H$_2$O$_2$ concentration. The addition of 0 to 50 mg/L H$_2$O$_2$ increased the degradation rate from 21% to 99.9% at 120 min of ozonation. The reaction process can be explained by the following equations, where in Equation (2), the conjugate base of the H$_2$O$_2$ concentration is pH dependent.

\[
\text{OH}^- + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2^- + \text{H}_2\text{O}_2 \quad (2)
\]

\[
\text{HO}_2^- + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_3^- \quad (3)
\]
The addition of H$_2$O$_2$ to O$_3$ results in O$_3$ decomposition and OH radical (∙OH) formation. At high pH, the concentration of HO$_2^-$ increases and hence the concentration of ∙OH increases [13]. At an acidic pH, ozone reacts selectively and slowly with organics, whereas with increasing pH ozone decomposition is accelerated and radical reactions occur via the reaction of ozone with some compounds known as initiators, such as hydrogen peroxide (H$_2$O$_2$) [16]. Reactions for O$_3$/H$_2$O$_2$ are similar to those for O$_3$ alone with added H$_2$O$_2$ dosing the system. The peroxone reaction is:

$$
\text{H}_2\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{HO}_2^- + \text{H}_3\text{O}^+ + \text{O}_3 + \text{HO}_2^- \rightarrow ∙\text{OH} + \text{O}_2^- + \text{O}_2. \quad (11)
$$

An increase in DEP degradation with the addition of H$_2$O$_2$ to the ozonation process was due to the formation of OH radicals. According to Figure 2, the optimal H$_2$O$_2$ concentration was ≈40 mg/L with almost complete DEP removal (99.9%). No additional decrease in DEP concentration was obtained with the addition of 50 mg/L H$_2$O$_2$ to the peroxone treatment.

Supplementary Figure S2 shows the change in pH during the peroxone process. During the ozonation treatment, the pH gradually decreased from 7.5 to 5.1 with time and with the addition of H$_2$O$_2$. Alkaline pH enhances the formation of OH radicals as more hydroxide ions are present (Equations (12) and (13)). These hydroxide ions initiate O$_3$ decay.

$$
\text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2. \quad (12)
$$

$$
\text{O}_3 + \text{HO}_2^- \rightarrow ∙\text{OH} + \text{O}_2^- + \text{O}_2. \quad (13)
$$

The produced ∙OH (Equation (13)) can subsequently introduce further chemical reactions with O$_3$, resulting in an increased OH radical formation. In addition, the pH of the wastewater influences the acid/base equilibria of some compounds, as well as the O$_3$ reaction rate.

3.2. Effect of O$_3$/H$_2$O$_2$ Process on COD, UVC, and pH

Leachate is characterized by a high concentration of organic matter, as determined by COD value, which refers to the amount of specific oxidant reacting with the sample under controlled conditions [17]. In this study, the initial COD value in the leachate was ≈16,400 mg/L. The mixed solid wastes that were deposited in the open dump in a non-segregating method produced a high COD and probably required a high concentration of oxidant to degrade the complex compounds and increase the leachate biodegradability. Figures 3 and 4 show the effects of O$_3$ and O$_3$/H$_2$O$_2$ on COD and the correlation between COD and UVC, respectively. Figure 3 illustrates that only 12.2% of the COD was removed, from 16,400 mg/L to 14,400 mg/L, during 120 min of O$_3$ treatment. The presence of H$_2$O$_2$ (5, 10, 20, 30, 40, and 50 mg/L) resulted in increased COD removal, from 15.9% (O$_3$/5 mg/L H$_2$O$_2$) to 68.9% (O$_3$/50 mg/L H$_2$O$_2$) for a final COD concentration after 120 min of ≈5800 mg/L. Removal of COD indicates that the addition of H$_2$O$_2$ increased the formation of OH radicals, which in turn mineralized the organic compounds. Tizouei et al. reported an improvement in COD removal from 27% to 48% using semi-batch O$_3$ and O$_3$/2000 mg/L H$_2$O$_2$, respectively [18], which was a considerably higher amount of H$_2$O$_2$ than that used in the present study.
Figure 3 shows that the COD decreased gradually during the initial O₃ and O₃/H₂O₂ processes due to the availability of OH radicals. Further, an increase in COD concentration was observed at 60 min (except for the O₃ treatment alone), indicating the formation of organic acids during DEP degradation by AOP [13]. As the peroxone treatment continued, COD decreased further due to additional oxidation of the intermediates by OH radicals to the final COD. The COD removal with 40 mg/L H₂O₂ was similar to that with 50 mg/L H₂O₂, showing that an increased H₂O₂ concentration does not always result in increased COD-removal rates. The increase in H₂O₂ concentration leads to a change in its role from OH radical producer to inhibitor of O₃ decomposition by free radicals [19].

According to Peretz et al. [16], increasing the concentration of H₂O₂ can cause further decomposition of ozone while yielding the ozonide radical anion O₃, which could be detected as dissolved ozone. This may result in a pseudo increase in the dissolved ozone concentration. Similarly, UVC at 254 nm followed the COD removal trend, probably due to its high concentration, for an optimum dosage of O₃/40 mg/L H₂O₂ (Figure 4).

Figure 4. COD versus UVC for O₃ with 40 mg/L H₂O₂.

Numerous studies have shown that UVC can be used to probe the micropollutant removal in secondary wastewater effluent, e.g., to track carbamazepine in a secondary effluent [20]. However, the current study showed that in the complex leachate matrix, it was not possible to track the degradation of the target pollutant using UVC. Leachate has many complex organic substances and heavy metals that interfere with pollutant removal, and Figure 4 proves that the UVC reflected the degradation of COD in leachate, indicating that it cannot be used as a tracking model for DEP removal.

3.3. Effect of t-BuOH in the Kinetic Evaluation

The radical scavenger t-BuOH was added to quench the formation of OH radicals during the ozonation process because the rate constant of O₃ for DEP is very low (K O₃ = 0.06 – 0.1 M⁻¹s⁻¹) and maximum DEP removal was achieved using the OH radicals. To determine the impact of direct ozonation on DEP degradation, t-BuOH was added to the leachate at 50 mM, 100 mM, 150 mM, and 200 mM. Figure 5 shows the removal of DEP in leachate with different concentrations of t-BuOH compared to the direct ozonation of the leachate. Ozonation alone yielded ≈21% DEP removal from the leachate (120 min; TOD = 4971 mg/L), whereas addition of t-BuOH to the leachate increased the removal rate of DEP instead of decreasing it.
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\[ O_3 + \text{HO}^- \rightarrow O_3^- + \text{HO}_2^- \]  \hspace{1cm} (14)

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![Figure 5. Diethyl phthalate (DEP) removal in leachate for different tert-butanol (t-BuOH) concentrations.](image-url)

From Figure 5, the addition of 50 mM t-BuOH gave 64.3% DEP removal; increasing the t-BuOH concentration to 150 mM resulted in less DEP removal (≈26.3%), and 200 mM t-BuOH then increased the DEP degradation to a final concentration of 12.6 mg/L after 120 min. Thus, even after the addition of
the OH radical scavenger, there was more degradation of DEP than with ozonation alone. The addition of t-BuOH surprisingly did not suppress the OH radical formation. Instead, the addition of t-BuOH enhanced the DEP removal in comparison to the ozone treatment without the added t-BuOH. t-BuOH may contribute to the formation of transesterification products, which in turn may enhance the OH radical’s formation [21] and the degradation of DEP. Transesterification is the process of exchanging the organic group of an ester with the organic group of an alcohol. Consequently, in the leachate matrix, t-BuOH cannot be used to evaluate the impact of direct ozonation on DEP degradation.

\[
\text{R'}\text{OH} + \text{R''O}_\text{R} \rightarrow \text{R'O}_\text{R} + \text{R''OH} \quad (15)
\]

### 3.4. OH Radical Exposure

O\(_3\) exposure \(\int [\text{O}_3] dt\) and OH radical exposure \(\int [\text{OH}] dt\), under the R\(_{ct}\) concept, were monitored during ozonation by the depletion rate of an in situ OH radical probe compound (pCBA). R\(_{ct}\) represents the ratio of the OH radical concentration to the O\(_3\) concentration in a given body of water/wastewater (R\(_{ct}\) = \([\cdot\text{OH}]/[\text{O}_3]\)) [22]. Degradation of pCBA in leachate can be predicted using the O\(_3\) kinetics and R\(_{ct}\). The OH radical and O\(_3\) exposures in a steady state are determined specifically for every application since they are directly affected by water-quality parameters:

\[
\frac{c}{c_0} = \exp\left(-k_{\text{O}_3} \int [\text{O}_3] dt - k_{\text{OH}} \int [\text{OH}] dt\right) \quad (16)
\]

where \(k_{\text{O}_3}\) represents the rate constant of O\(_3\) and \(k_{\text{OH}}\) represents the rate constant of OH radicals for the O\(_3\) probe compound pCBA. The direct reaction of the resistant tracer with O\(_3\) is negligible; hence its contribution to compound removal can be eliminated from the equation, according to Equation (15). The “OH-radical probe method” involves an indirect determination of oxidant exposures, where the OH radical exposure is back-calculated from the removal of the O\(_3\)-resistant probe compound (pCBA) [22–25]:

\[
\frac{c}{c_0} = \exp\left(-k_{\text{OH}} \int [\text{OH}] dt\right) \quad (17)
\]

However, an accurate O\(_3\)-exposure measurement in wastewater effluent is problematic since the rapid reaction of effluent organic matter and even effluent particles [20] with O\(_3\) results in rapid O\(_3\) depletion in the first milliseconds of the reaction [23]. An alternative concept, referred to here as the “O\(_3\) probe method,” suggests that O\(_3\) exposure can be back-calculated from the removal of an internal tracer (a moderately or rapidly reacting probe compound) that reacts with both O\(_3\) and OH radicals following the ozonation of wastewater effluents. DEP cannot be used as the internal probe compound for OH radical estimation due its degradation to both superoxide and peroxy radicals [26].

Using the R\(_{ct}\) concept, the OH radical probe compound pCBA was spiked into the leachate (at 10 mg/L and 20 mg/L) containing 20 mg/L DEP, and its final concentration was determined after ozonation for different time intervals (Figure 6). Table 2 shows the OH exposure for 10 and 20 mg/L pCBA, respectively; with \(K_{\text{O}_3}\) and \(K_{\text{OH}}\) values for the O\(_3\) treatment of 0.15 M\(^{-1}\)s\(^{-1}\) and 5 \(\times\) 10\(^9\) M\(^{-1}\)s\(^{-1}\).
3.5. Formation of Intermediate Transformation Products

DEP degradation contributes to the formation of various byproducts during the O₃ and O₃/H₂O₂ treatment processes, along with the production of organic acids, such as succinic acid, malonic acid, and glutaric acid [13], as well as three possible intermediate products: phthalic acid, 4-hydroxy phthalic acid, and phthalic anhydride [13]. Figures 7 and 8 show the trend analysis of the areas for phthalic acid and 4-hydroxy phthalic acid, respectively. Intermediate product formation occurs upon DEP degradation due to cleavage of its chain and hydroxylation of the aromatic ring.

Previous studies have shown that during ozonation [10], DEP does not readily react with O₃ molecules, indicating a very low reaction-rate constant. Consequently, O₃ decay via DEP degradation results in the formation of intermediate DEP-oxidation products. During the 120-min O₃ treatment, there was a consistent increment of phthalic acid (Figure 7), while 4-hydroxy phthalic acid was not produced using O₃ alone (Figure 8), possibly due to a low concentration or absence of OH radicals that are expected to attack the aromatic ring at the para position.
In addition, Figures 7 and 8 show that the areas of both phthalic acid and 4-hydroxy phthalic acid increased during the first 60 min of the O$_3$/H$_2$O$_2$ treatment. As the treatment time increased, the intermediate products increased during the DEP degradation, reaching a maximum area, and then began to decrease as the experiment proceeded. Figure 7 shows that the area of phthalic acid decreased after 120 min while there was still residual phthalic acid in the leachate. 4-Hydroxy phthalic acid showed the same trend and there was a complete elimination of 4-hydroxy phthalic acid, except with 5 and 20 mg/L H$_2$O$_2$ after 120 min (Figure 8). Table 3 shows the second-order reaction rate constants for the O$_3$ and OH radical with DEP.
Table 3. Second-order rate constants for the reaction of O₃ and OH radicals with diethyl phthalate.

| Compound Name        | Structure | K_O₃ (M⁻¹s⁻¹) | K_OH (M⁻¹s⁻¹) |
|----------------------|-----------|---------------|---------------|
| Diethyl phthalate    | ![Structure](image) | 0.06–0.1 (Wen et al., 2011) | 3–5 × 10⁹ (Haag et al., 2005) |

4. Conclusions

The degradation of DEP by O₃ alone and peroxone with varying concentrations of H₂O₂ was demonstrated. The simulated leachate had a high concentration of COD (16,400 mg/L) along with heavy metals, resulting in a complex matrix for the treatment process. DEP was not degraded by O₃ alone [27], but it was degraded by the peroxone process due to the high rate removal by OH radicals (3.9 × 10⁹ M⁻¹s⁻¹). The COD removal of DEP by O₃ with 40 mg/L H₂O₂ showed a 65% decrease in 120 min from the initial COD. Measurement of the in-gas and off-gas O₃ dose during the treatment process revealed a rapid kinetic change in the initial treatment time that decreased toward the end of the treatment and influenced the oxidation process. The ozonation of leachate resulted in a minor change in pH due to the buffering effect of the bicarbonates. The OH radical exposure in a steady state was estimated using a radical probe compound, which confirmed the OH radical’s reaction with the leachate and its effect on the contaminant degradation. Two intermediate products were detected using HPLC–MS during the DEP degradation: phthalic acid and 4-hydroxy phthalic acid. They were confirmed using available reference compounds and ESI (+) MS spectra. A trend analysis was performed to estimate their area and degradation during the treatment process.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1944/12/4/4119/s1, Figure S1. Transferred ozone dosage; Figure S2. Influence of O₃ and O₃/H₂O₂ on pH.

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