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Combined Application of Ozone and Hydrogen Peroxide to Degrade Diesel Contaminants in Soil and Groundwater

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Abstract: Environmental pollution has been a major concern in recent times, and soil and groundwater pollution are areas which have received particular focus. This has led to the development of various remediation techniques such as excavation, soil vapor extraction, bioremediation, chemical oxidation, and so on. Among all remediation techniques, chemical oxidation has been proven to be the most effective and feasible technique around the world. In this study, various combinations of ozone and hydrogen peroxide were used to treat diesel-contaminated soil and groundwater in an experimental setup. Experimental soil and groundwater were prepared with properties similar to the contaminated soil. An ozone generator and a pump injection system were deployed for combining ozone and hydrogen peroxide. Five different experiment batches were prepared based on the hydrogen peroxide concentration and its ratio to the soil. The diesel concentration in the water dropped from 300 mg/L to 7 mg/L in the first hour of treatment, which dropped below the detection limit (0.01 mg/L) thereafter. Similarly, 63.9% degradation was achieved with the combined sparging of ozone and hydrogen peroxide in the soil. Ozone combined with 7% hydrogen peroxide was the most promising combination for removing the contaminants. In addition, this research explored the hydroxyl radical conversion rate of ozone and the perozone, the difference in order of magnitude is greater than one which shows that the perozone has better oxidation capacity than ozone only. The findings of this study show that combining ozone with hydrogen peroxide is a competent and feasible onsite remediation method for diesel contaminants in soil and groundwater. Thus, this method can be applied in local gas stations, accidental spillage sites, and small-scale refineries for onsite treatment in a cost-effective and technically sound way within a short time span.



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1. Introduction

Soil is home to thousands of species and billions of populations [1]. It plays a pivotal role in ecosystem regulation and support [2–4]. Most species, including human beings, depend on soil in one way or another for food and habitat [5]. However, in recent years, soil, along with groundwater, has been contaminated by numerous anthropogenic activities altering its physical and chemical properties. This has serious effects on the biogeochemical cycles [6–8].

The emerging technologies that are replacing hydrocarbon-based fuel are revolutionizing the world, yet diesel-based fuels serve as the most commonly used fuel source in transportation and industries and will take years for complete replacement [9]. This fuel source contributes massively to soil and water pollution, as well as air pollution. Oil spills during transport and transfer, industrial wastewater, underground fuel reserve tanks, vehicle service centers, etc., are major sources of diesel contamination in soil and water [10]. The accidental spillage from oil transport tankers is another cause of local soil and groundwater

pollution in the countries where there are no underground pipeline facilities. Gas stations and small-scale oil refineries discharge diesel-based wastes improperly, for example, in Sulaymaniyah city, Iraq [11]. Thus, the above-mentioned factors are the major sources of diesel contamination in soil which increases the soil carbon, causing an imbalance in the soil nutrient, resulting in the ecological destruction of the environment, ecology, and human health [12–15].

Due to the continuous operation of the above-mentioned leaking sources and space constraints, in situ remediation is desired [10]. The trend of using advanced oxidation processes and bioremediation for diesel contamination has been increasing in recent years because of its higher efficiency and lower environmental impact. The oxidants widely used for this process include hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), ozone (O_3), persulfate ($\text{S}_2\text{O}_8^{2-}$), and Fenton process ($\bullet\text{OH}$). These oxidants convert the organic pollutants either to harmless or less harmful compounds, thereby positively impacting the soil and the environment [16–19].

During the advanced oxidation process, the uniform distribution of oxidants is less likely. When gaseous ozone is used only for oxidation, a high concentration of dysoxidizable contaminants cannot be effectively degraded because of its limited oxidation capacity. The ozone molecule, in contrast, is easily oxidized to hydroxyl radicals ($\bullet\text{OH}$) with strong oxidizing power under the catalysis of hydroxyl ion and it has a redox potential of 2.80 volts [20–22], which is higher than the ozone molecule. A free radical reacts with organic matter mainly through three mechanisms: hydroxy addition, hydrogen abstraction, and electron transfer [23]. Generally, the reaction of the free radicals and organic matters is not selective [24], and besides the oxidation of the compound with an unsaturated bond, the free radicals react with an aliphatic compound with an unsaturated bond. However, during free radical chain reaction, it is easy to react with radical scavengers, such as carbonate, bicarbonate, etc., which hold a great reaction rate with the hydroxyl radicals, thus causing an inhibiting effect on the free radical chain reaction [25].

If gaseous ozone is combined with liquid hydrogen peroxide for chemical oxidation, mutual intensification may produce plenty of hydroxyl radicals to improve their oxidation capacity [26]. Therefore, the perozone reaction is made by combining the ozone with the hydrogen peroxide, and their chemical oxidation capacity is improved by injecting the ozone into the saturated zone and hydrogen peroxide into the unsaturated zone. Therefore, reaction time may be shortened by the production of plenty of hydroxyl radicals during the perozone reaction to improve the contaminant degradation rate and reduce the required ozone [27,28].

Several prior studies have focused on the technique of using ozone and hydrogen peroxide for oxidation-reduction to treat diesel contaminants in soil and water [29–32]. There are diverse studies that report the combination of these two to treat various pollutants [33–35], while limited studies are focused on soil and water treatment [36]. Thus, this study was carried out to determine the effectiveness of diesel degradation in soil and groundwater using various proportions of hydrogen peroxide combined with ozone. Our study assumes that the experimental setup characterizes the physio-chemical properties of the soil and water at the actual contaminated site. The findings of this study will establish a strong stand for policymakers and concerned personnel to establish an onsite remediation setup that is economically feasible and technically sound.

2. Materials and Methods

2.1. Experimental Procedure and Design

Diesel contaminated soil and groundwater samples were collected from one of the contaminated sites in central Taiwan. The samples were analyzed to determine their chemical and physical properties. Experimental soil was prepared with similar chemical and physical properties since soil from the contaminated site was not permitted to collect in large quantities. A high-density polyethylene (HDPE) tank with a volume of $2.83 \times 10^5 \text{ cm}^3$ was built and was equipped with a good casing and screen at the center. The

tank was then filled with 150 kg of artificially contaminated soil [37] and 57 L of water to form a saturated layer (Figure 1). Then, the top of the contaminated soil was covered with non-contaminated soil and the tank was sealed with ethylene propylene diene monomer rubber.

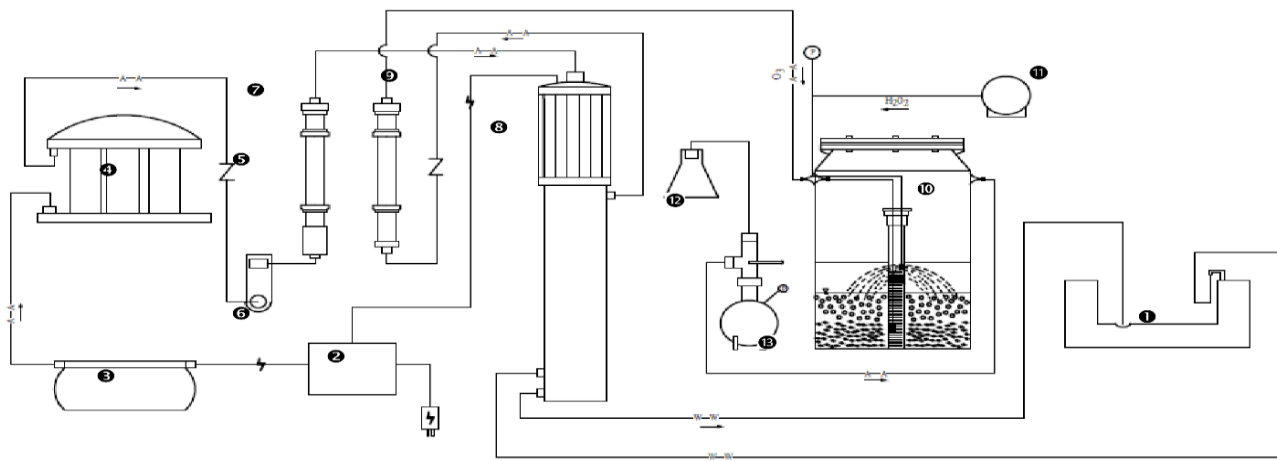


Figure 1. Schematic diagram experimental setup. (1) Cooling water tank; (2) High voltage transformer; (3) Air compression pump; (4) Oxygen generator; (5) Check valve; (6) Flow control valve; (7) Oxygen flow meter; (8) Quartz electrode; (9) Ozone flow meter; (10) Reaction tank; (11) Pump; (12) KI solution; (13) Air compressor.

Ozone gas used in the experiment was generated in the laboratory using an ozone generator (EMEC, OXL-50) which uses a quartz tube discharge method. In this method, atmospheric air is used instead of pure oxygen, which results in the formation of trace nitrous oxide influencing the pH of the water [38]. Similarly, a pump injection system was established to inject hydrogen peroxide into the sample soil.

2.2. Operating Conditions of Ozone and Hydrogen Peroxide Reaction System

A preliminary study was conducted with different flow rates, viz. 5 L/min, 7.5 L/min, 10 L/min, 15 L/min, and 18 L/min to determine the optimum production (288 mg/L at 10 L/min) and minimum emission (8 h moving average, 0.04 ppm). Thus, the ozone with a concentration of 288 mg/L was sparged into the sampling tank for 1 h with a flow rate of 10 L/min. The sample was taken after 23 h for analysis and this process was carried out 12 and 24 times. The experiment was conducted with five different settings based on the use of hydrogen peroxide concentration and its ratio to the soil by weight (Table 1). Three different concentrations of hydrogen peroxide (4%, 7%, and 10%) and two different H₂O₂ and soil weight ratios (1:50 and 1:100) were used in this study. The three different H₂O₂ concentrations were experimented with the same H₂O₂:soil ratio (1:50), one sample with ozone only, and the remaining sample with 7% H₂O₂ in 1:100 H₂O₂:soil ratio (Table 1). The experiment was repeated 24 times for two combinations viz. soil treated with ozone only and ozone with 7% H₂O₂ and 1:100 H₂O₂:soil ratio (Batch 1 and 5) and the rest were treated 12 times (Batch 2, 3, and 4).

Table 1. The different experimental scenarios used in the study.

Initial Diesel Concentration (mg/kg)	Experiment ID	H ₂ O ₂ Concentration	H ₂ O ₂ :Soil Ratio (Weight Basis)
24,200	Batch 1	0%	x
24,223	Batch 2	4%	1:50
17,115	Batch 3	7%	1:50
14,286	Batch 4	10%	1:50
32,131	Batch 5	7%	1:100

2.3. Sampling and Analysis

The soil sample was taken from distances of 5 cm, 15 cm, and 30 cm from the central gas injection tube. Then the sample was mixed well to maintain homogeneity. The residual diesel concentration and pH of the soil were analyzed before and after the treatment. Similarly, pH, residual diesel concentration, oxidation-reduction potential (ORP), and conductivity of groundwater were also analyzed. All the samples were tested three times and the mean was used in the results [39]. The major component of diesel fuel included straight-chain hydrocarbons (C10–C25) and branched-chain hydrocarbons, such as pristane and phytane. Therefore, the effectiveness of the hydrogen peroxide and ozone treatment system was analyzed based on overall diesel-range, total petroleum hydrocarbons (TPH-d), C13, C17, pristane, C18, phytane, and C23 degradation. The Mann Kendall trend test, which is a non-parametric statistical test that does not require the sample to follow a definite distribution pattern, was used to analyze the degradation of diesel over time [40–42].

The concentration of TPH-d was measured using a gas chromatograph (GC) (Perkin Elmer Clarus 500) with GS-Alumina columns (30 m × 0.32 mm × 0.1 μm, Agilent) and a flame ionization detector. Ultra-high purity grade nitrogen (99.999%) was used as the carrier gas and supplemental gas in the analysis at a flow rate of 30 mL/min. The temperatures of the injection port and detector were 300 °C and 330 °C, respectively, which was increased from 50 °C at a controlled rate of 10 °C/min. The final temperature was maintained for 7 min. The analysis and QA/QC were carried out according to Taiwan Environmental Protection Agency (Taiwan EPA) procedures (NIEA S703.62B) [43]. The precision and accuracy were determined by triplicate analysis of QC samples at low (1250 mg/L) and high (25,000 mg/L) concentrations by overall mean, relative standard deviation (% RSD), and percent deviation (% DEV). The % RSD for precision was comprised below 10.6%, and % DEV for accuracy was between 3.0 and 7.0%.

2.4. Hydroxyl Radical Conversion Rate

This study has explored the conversion rate of hydroxyl radicals after reacting with ozone and a combination of both ozone and hydrogen peroxide, this combination hereafter is referred to as the perozone. For this experiment, the ozone flow rate, concentration, and mass flow rate were maintained at 5 L/min, 1.94 mg/L, and 9.702 mg/min. For the perozone study, 1 mL of 7% hydrogen peroxide was added to the experimental setup before ozone sparging. Since hydroxyl radical ($\bullet\text{OH}$) is difficult to detect, 4-Chlorobenzoic acid (*p*CBA) was used as a probe compound. 4-Chlorobenzoic acid (*p*CBA) reacts easily with hydroxyl radical ($\bullet\text{OH}$) and does not react with ozone, making the detection facile. The initial concentration of *p*CBA was 10 mg/L, which was fully reacted in 70 s. The reaction mechanism is given in Equations (1)–(3) [44].

$$\frac{-d[p\text{CBA}]}{dt} = k_{\bullet\text{OH}/p\text{CBA}} [p\text{CBA}][\bullet\text{OH}] \quad (1)$$

where, $k_{\bullet\text{OH}/p\text{CBA}}$ is reaction rate constant whose value is $5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, and ozone and $\bullet\text{OH}$ reaction pathway can be predicted by ozone reaction kinetics and the ratio of hydroxyl radical exposure to ozone exposure (R_{ct}); R_{ct} can be expressed as in Equation (2).

$$R_{ct} = \frac{\int [\bullet\text{OH}] dt}{\int [\text{O}_3] dt} \quad (2)$$

where $\int [\text{O}_3] dt$ is ozone concentration over time. Substituting Equation (1) into Equation (2), the following Equation (3) was obtained. Thus, using Equation (3), R_{ct} was calculated and oxidation capacity was determined.

$$\ln\left(\frac{[p\text{CBA}]}{[p\text{CBA}]_0}\right) = -k_{\bullet\text{OH}/p\text{CBA}} R_{ct} \int [\text{O}_3] dt \quad (3)$$

3. Results and Discussion

3.1. Background Investigation

The sample soil and groundwater were taken from a polluted site in central Taiwan. The results of soil texture analysis showed that the soil was composed of 75% sand, 15% silt, and 10% clay and, thus, is classified as sandy loam by the United States Department of Agriculture (USDA). Similarly, the bulk density, porosity, and hydraulic conductivity of the soil were 1.58 g/cm^3 , 41%, and $1.071 \times 10^{-3} \text{ cm/sec}$, respectively. The diesel concentration in the contaminated soil and groundwater was found to be 1600 mg/kg and 45 mg/L, respectively. To determine the effect of perozone on diesel degradation, diesel was sprinkled in the soil and groundwater to achieve an initial diesel concentration between 14,000 and 32,131 mg/kg in the soil and 300 mg/L in the groundwater. Constant concentration could not be achieved since the concentration of diesel kept fluctuating over time [39].

3.2. Effect of Ozone and Perozone on Oxidation-Reduction Potential of Groundwater

In this study, contaminated groundwater was treated with ozone only and with perozone in different soil ratios (Table 1) to observe the effect on ORP. The ORP value of the Batch 1 sample spiked from -138 mV to 247 mV in the first hour, which descended after 3 h, then increased to 257 mV and showed a gradual increment reaching the value of 276 mV in the last 12 h (Figure 2). There was a gradual increment in the ORP value for Batch 5 for the first 3 h from 250 mV to 559 mV which then decreased gradually to 514 mV . The values were inconsistent for the remaining batches with the increased final values. Thus, it was observed that the ozone only treatment could quickly increase the ORP compared to the perozone treatment. For the perozone treatment, the highest efficiency can be achieved within the first 4 h of treatment. The greater the ORP, the stronger the oxidation potential, thus, the higher the efficiency of organic pollutants removal [45].

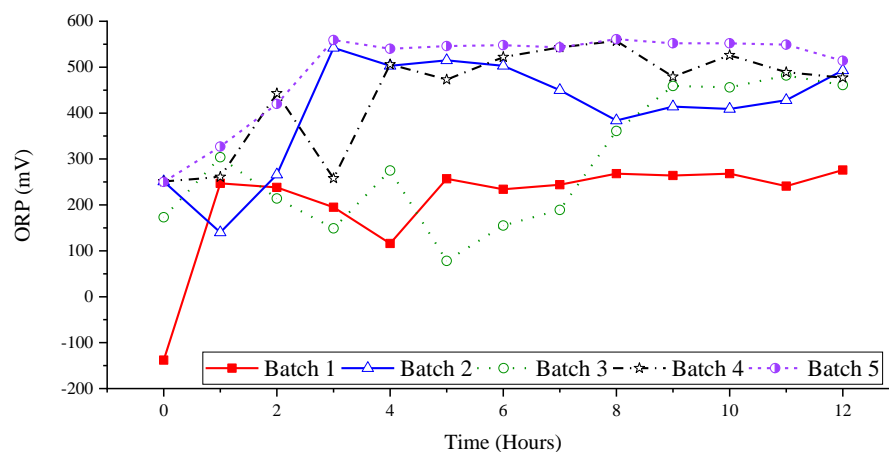


Figure 2. Effect of ozone and perozone on ORP of groundwater over time.

3.3. Effect of Ozone and Perozone on pH Value of Groundwater

Groundwater was treated with ozone and perozone to understand the effect on pH. The results showed that the groundwater was acidified in the first hour of treatment in all the batches. There was a fluctuation in the pH value after 8 hours of treatment in Batches 1, 3, and 4, whereas in the remaining batches, the pH value was almost constant until 12 h. However, the pH after 12 h of treatment was almost equal to all the batches (Figure 3). The ozone has high ORP and thus oxidizes the organic matter forming organic acids, aldehydes, and ketoacids. This mechanism increases the acidity of water, resulting in the decrease in the pH [46,47].

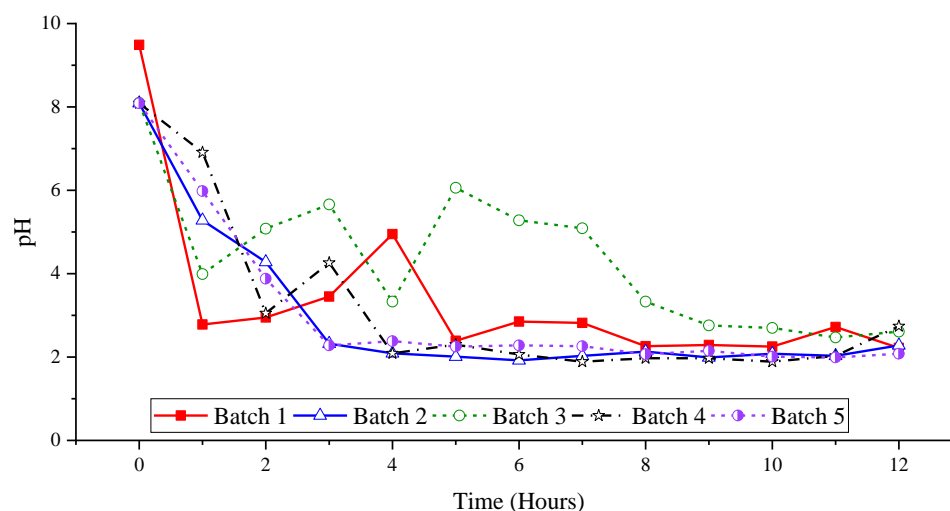


Figure 3. Effect of ozone and perozone sparging on pH value of groundwater.

The anion concentration of the groundwater collected from the contaminant site was analyzed using ion chromatography with a conductivity detector after 1 and 6 h of treatment with ozone (Table 2). There was a high increase in nitrate, chloride, fluoride, and sulfate ion concentration after the ozone treatment, which lead to a decrease in the pH value. Since this system used the ozone purified by separating nitrogen from the air, the remaining nitrogen may have formed trace nitrogen oxide. The results show that the acidification of groundwater after ozone injection was because of the generation of a high concentration of nitrate ions. The 100 L reaction tank used in this study may have caused the accumulation of nitrate ions in the groundwater due to the production of nitrogen oxides in the experimental system.

Table 2. Anion concentration before and after ozone sparging in the groundwater.

Items	Groundwater w/o Ozone Sparging (mg/L)	Groundwater after 1 h Ozone Sparging (mg/L)	Groundwater after 6 h Ozone Sparging (mg/L)
pH	9.49	2.85	2.22
Br ⁻	<0.01	<0.01	<0.05
BrO ₃ ⁻	<0.0006	<0.0006	<0.0006
NO ₃ ⁻	0.80	380	1090
PO ₄ ³⁻	0.50	<0.013	0.60
Cl ⁻	6.80	9.80	20.2
F ⁻	<0.013	0.50	1.00
SO ₄ ²⁻	5.20	14.8	71.5
NO ₂ ⁻	<0.011	1.00	1.90

3.4. Effect of Ozone and Perozone on Diesel Degradation of Groundwater

The effect of ozone and different combination of perozone was investigated in this study. The diesel concentration of groundwater dropped significantly within the first hour of ozone treatment. The diesel contaminant remained undetected in Batches 4 and 5 during the first hour. In Batch 1, there was an inconsistency in the TPH-d concentration whereas, in Batch 3, the concentration decreased from 300 mg/L to 7 mg/L in the first hour and then remained below the detection limit throughout the testing time. In Batch 5, the concentration was below the detection limit from the first hour of sparging (Figure 4). After 12 h, the concentration of TPH-d was below the detection limit. The detection limit of the instrument was below 0.01 mg/L. The result shows that perozone is effective at treating diesel contaminants in groundwater in a short time span. This result is achieved by the higher reaction rate between hydroxyl radical and diesel hydrocarbons. The finding of this

study is supported by Kong et al.'s study [48] which recommended further study on the ratio for use of H₂O₂ and O₃.

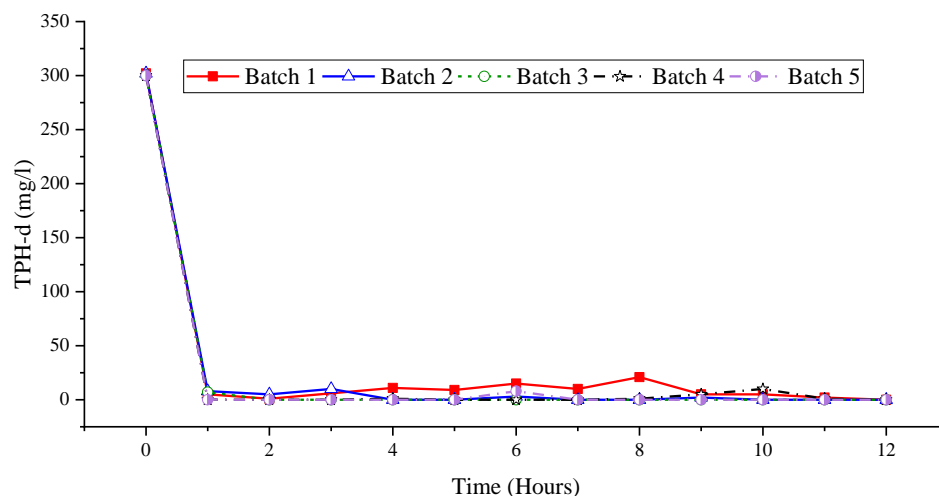


Figure 4. Degradation of diesel in groundwater over time by ozone and perozone sparging.

3.5. Effect of Ozone and Perozone in Diesel Contaminated Soil

The diesel degradation in the soil was analyzed on a decreased TPH-d concentration basis. None of the batches showed a regular trend in diesel degradation (Figure 5). There was inconspicuous degradation of diesel contaminant in Batches 1, 2, and 4 (37.27%, 37.22%, and 36.96%, respectively), whereas copious degradation was found in Batches 3 and 5 (63.9% and 62.69%) after 12 h of ozone and perozone sparging. The efficiency of diesel degradation was increased by 15.13% in Batch 5 when the sparging time was increased to 24 h whereas, in Batch 1, the efficiency was increased by 20.57%. Hence, the highest degradation rate was achieved in Batch 3, which is the combination of ozone and 7% H₂O₂ concentration with H₂O₂:soil ratio 1:50. Thus, this provides the optimum ratio of H₂O₂ and soil with O₃ combination for effective removal of diesel contamination from soil. The mechanism which supports this result is supplemented by the results of Bourgin et al., which state that the excessive hydroxyl ion is produced during the reaction and reacts with each other to become stable H₂O₂ [36].

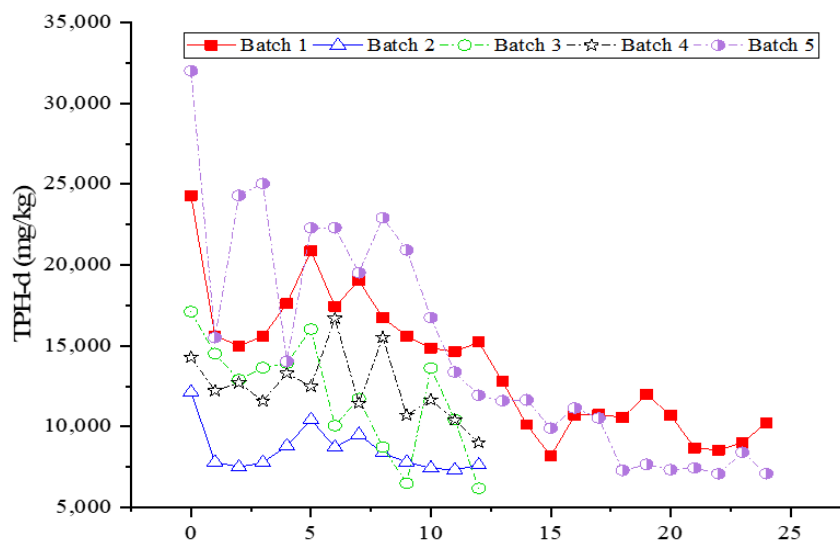


Figure 5. Degradation of diesel (TPH-d concentration) in soil by ozone and perozone treatment.

3.6. Effect of Ozone and Perozone in C13, C17, Pristane, C18, Phytane, and C23 Degradation

The degradation effect on the specific hydrocarbons in diesel, such as C13, C17, pristane, C18, phytane, and C23 components, were analyzed by ozone and perozone sparging, and the degradation efficiency is expressed by the variation trend of the relative concentration of individual components. The testing results of ozone sparging (Batch 1) are shown in Figure 6a. A good degradation effect on all straight-chain hydrocarbons was observed by ozone sparging during the first hour, whereas branched-chain hydrocarbons such as pristane (Pr) and phytane (Ph) could not be degraded even after 15 h of sparging.

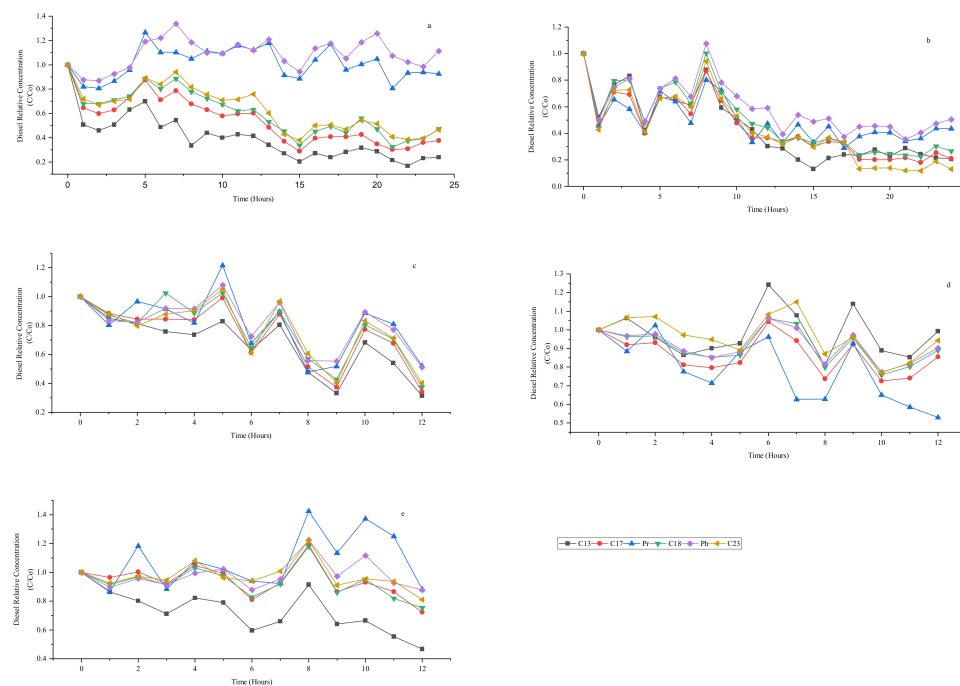


Figure 6. Change of relative concentration of specific hydrocarbons after treatment, Batch 1 (a), Batch 5 (b), Batch 3 (c), Batch 2 (d), and Batch 4 (e).

In the first hour of perozone sparging, Batch 5 showed a good efficiency for both branched and straight-chained hydrocarbons degradation. The relative concentration of hydrocarbons was 0.42 after 12 h and 0.29 after 24 h, showing significant degradation of hydrocarbons (Figure 6b). In Batch 3, there was gradual oxidation of hydrocarbons and they were degraded by perozone sparging concerning time. The relative concentration of hydrocarbon ranged between 0.31 and 0.52 after 12 h of the perozone treatment (Figure 6c). In Batches 2 and 4, an inconspicuous degradation effect was observed on hydrocarbon with an average relative concentration of 0.75 and 0.85, respectively, after 12 h of treatment (Figure 6d,e).

3.7. Hydroxyl Radical Conversion Rate (R_{ct})

The degradation of *p*CBA concentration in the ozone and perozone during the hydroxyl radical conversion is shown in Figure 7. The experimental data was used to determine the hydroxyl radical conversion rate (R_{ct}) for ozone and perozone using Equation (3). The R_{ct} for ozone was 5.18×10^{-10} , whereas there was an order difference in magnitude for the perozone (5.35×10^{-9}). Thus, the difference in R_{ct} value shows that the perozone has a higher oxidation capacity, and thus, provides better degradation of diesel contaminants.

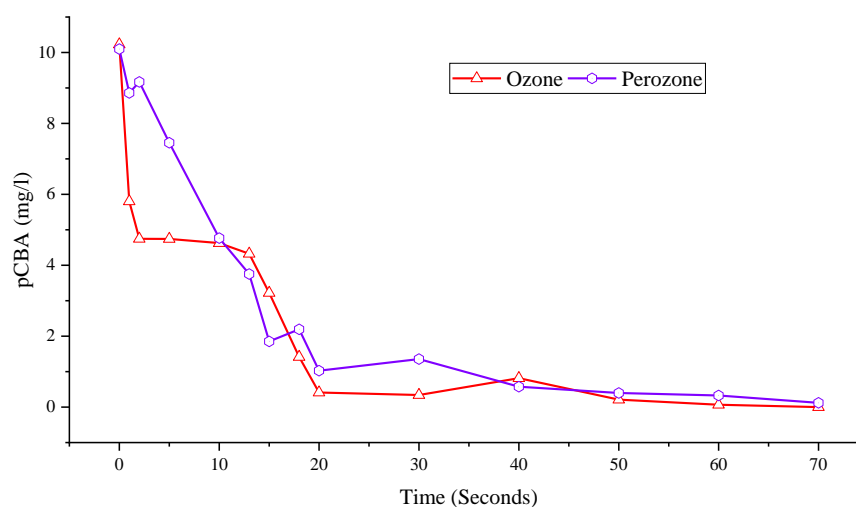


Figure 7. pCBA concentration with respect to ozone sparging time.

4. Conclusions

Diesel-contaminated soil and groundwater were treated with ozone and perozone at a laboratory-scale to assess the effectiveness of the removal of contaminants. The results showed that the oxidation capacity of perozone is better than ozone and can be effectively used for treating diesel contaminants in soil and groundwater simultaneously. Moreover, the findings indicated that groundwater can be treated with higher efficiency compared to soil with the same composition of perozone.

The experiment was conducted as a pilot study with 150 kg of soil and 57 L of water samples and showed promising results. The total estimated cost of the treatment was USD 1.95. Thus, this method is cost-effective, easy to install, and portable since it uses a small operating area, short duration, and minimal resources. This study shed light on the potential application on onsite contaminated areas such as accidental oil spillage, gas station leakage, small-scale refineries, etc.

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