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Remediation of Polycyclic Aromatic Hydrocarbon-Contaminated Soil Using Microwave-Activated Persulfate Oxidation System

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Abstract: Intensive industrial activities have led to severe polycyclic aromatic hydrocarbon (PAH) contamination of adjacent lands. Remediating such contaminated soil is crucial for maintaining long-term ecological health and sustainable development. This study systematically assessed the performance of a microwave-activated persulfate (MW/PS) oxidation method in remediating pyrene-contaminated soil. Under conditions of 80 °C and a persulfate concentration of 23.8 mg/g, this system achieved 85.3% pyrene degradation within 30 min, significantly outperforming both single microwave and thermal-activated persulfate (TH/PS) systems. Key factors influencing the oxidation efficiency included the temperature, persulfate and pyrene concentrations, moisture, and humic acid content. An electron paramagnetic resonance analysis confirmed the generation of reactive oxygen species, including $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $^1\text{O}_2$, in the MW/PS system, while $\text{O}_2^{\bullet-}$ was exclusive to the TH/PS system. However, further experiments revealed that $^1\text{O}_2$ had a negligible impact on pyrene degradation, suggesting that its role may have been overestimated in previous studies. The high MW/PS performance was attributed to the synergistic effects of both thermal and non-thermal (molecular vibration) mechanisms. Based on these findings, the pathways of pyrene degradation were proposed, with intermediate products exhibiting reduced toxicity and bioaccumulation potential. This study provides valuable insights into the application of MW/PS systems in the remediation of PAH-contaminated soils.

Keywords: advanced oxidation; microwave; persulfate; pyrene; remediation; soil



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused aromatic rings with varying structural configurations. These compounds are primarily produced through industrial processes, such as fossil fuel combustion and the incomplete incineration of organic matter [1]. Due to their high toxicity, persistence, and bioaccumulative properties, environmental agencies worldwide classify PAHs as priority pollutants. Exposure to PAHs has been linked to carcinogenic, teratogenic, and mutagenic effects in humans [2]. Their resistance to degradation and low bioavailability exacerbate environmental risks, as PAHs can accumulate and persist in soils, posing long-term contamination challenges [3]. Currently, soil contamination by PAHs remains a critical global environmental issue. In China, the most heavily contaminated sites are typically located near petroleum refineries, steel plants, and coking facilities, with maximum PAH concentrations in soil reaching up to 12.56 mg/g [4]. In the United States, PAH

contamination is responsible for 40% of the 1408 heavily polluted sites listed by the Environmental Protection Agency [5]. Addressing the remediation of these PAH-contaminated sites has become a key environmental priority in recent years, which could benefit long-term ecological health and sustainable development.

The remediation of PAH-contaminated soils mainly involves physical, chemical, and biological methods [6]. Physical methods, such as soil washing, are often inefficient and can generate significant volumes of wastewater. Biological methods are environmentally friendly and cost-effective, while they are challenged by a low degradation efficiency and are often combined with chemical methods as a pretreatment to enhance PAH bioavailability. Hence, chemical methods, primarily those based on advanced oxidation processes, play irreplaceable roles in most cases. Amongst various chemical methods, persulfate-based oxidation has garnered increasing attention in recent years. Compared to other oxidation processes, such as Fenton and ozonation, this method offers distinct advantages, including high efficiency, broad pH adaptability, and versatile activation pathways [7]. Upon activation, persulfate generates reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$) and sulfate radicals ($\text{SO}_4^{\bullet-}$), which can significantly drive the degradation of PAHs [8,9]. Common activation methods include thermal, transition metal, alkaline, and ultrasonic approaches [10–14]. While these methods have demonstrated varying degrees of success, their practical applications are constrained by many operational drawbacks, such as high energy demands, metal leaching, and disruption of the soil matrix. For instance, thermal activation suffers from a low activation efficiency and poor energy utilization [15], while transition metal and alkaline activation can change the physicochemical properties of the soil [16]. Therefore, advancing innovative and sustainable activation strategies is essential for enhancing the remediation efficiency and minimizing adverse environmental impacts.

The microwave-activated persulfate (MW/PS) system has garnered substantial interest in soil remediation due to its exceptional selectivity, rapid reaction kinetics, and energy efficiency. As a form of electromagnetic radiation, microwaves interact preferentially with polar molecules, such as H_2O and $\text{S}_2\text{O}_8^{2-}$, inducing rapid dipole rotation and localized heating [17,18]. This dual thermal and non-thermal effect not only increases system temperature but also destabilizes the persulfate O-O bond, generating ROS such as $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, which are effective in pollutant degradation [17]. Recently, several studies have explored the use of the MW/PS system in removing certain micro-pollutants from soil, demonstrating higher efficiency than conventional thermal-activated persulfate (TH/PS) systems. For instance, Peng et al. reported far faster phenanthrene removal using the MW/PS system than water bath heating activation, achieving nearly complete degradation within 30 min [19]. Similarly, Qu et al. demonstrated that the MW/PS system degraded organophosphorus pesticides 3–5 times faster than thermal activation, highlighting its superior kinetic efficiency [20]. Furthermore, incorporating transition metals, such as iron and manganese oxides, into the MW/PS system can further enhance the degradation efficiency [5,21]. The results of these studies highlight the promising potential of the MW/PS system for effective soil remediation.

The activation of persulfate is broadly categorized into radical ($\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, and $\text{O}_2^{\bullet-}$) and non-radical ($^1\text{O}_2$) pathways [22]. However, the mechanism underlying microwave activation of persulfate remains unclear, as various studies have reported inconsistent findings regarding the ROS generated in the system. For instance, Miao et al. suggested that the MW/PS oxidation of ethyl parathion in soil primarily relied on $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ [23]. However, Qu et al. suggested additional contributions from $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ in the same system [20]. Further complicating the picture, Wu et al. identified four ROS ($\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$) in an iron oxide-enhanced MW/PS system for PAH removal [21], while a manganese oxide-modified MW/PS system generated only $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, and $^1\text{O}_2$ [5].

Additionally, Shang et al. reported that the degradation of 4-chloronitrobenzene in an MW/peroxymonosulfate system was primarily driven by $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, with $^1\text{O}_2$ showing negligible activity [24]. These varying results underscore the lack of consensus on the ROS involved in the MW/PS system, presenting challenges for further advancing this technology.

Generally, the PAHs containing 4–7 fused aromatic rings exhibit higher toxicity and greater resistance to degradation than those with 2–3 rings [25]. This study investigated the degradation of pyrene, a common PAH containing four rings, in soil using the MW/PS system, with three principal objectives: (1) to examine the key factors (temperature, persulfate and pyrene concentrations, moisture, and humic acid) influencing the performance of the MW/PS system; (2) to compare the MW/PS and TH/PS systems, quantify efficiency enhancements, and differentiate thermal and non-thermal effects; (3) to elucidate the degradation mechanisms and determine the contributions of different ROS in the MW/PS system. This research enhances the fundamental understanding of the MW/PS system and provides valuable insights for its scalable and sustainable application in soil remediation.

2. Materials and Methods

2.1. Chemicals

Pyrene and n-hexane were purchased from MERYER Co., Ltd., Shanghai, China. Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), tert-butanol (TBA), and hydrogen peroxide (H_2O_2 , 30%) were purchased from Jiaoziteng Co., Ltd., Nanjing, China. Sodium sulfate, dichloromethane, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), and 1,4-benzoquinone (BQ) were purchased from Titan Technology Co., Ltd., Shanghai, China. Acetonitrile, Methyl alcohol (MeOH), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Juyou Scientific Equipment Co., Ltd., Nanjing, China. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMP) was purchased from Zhongdonghuabo Co., Ltd., Nanjing, China. Sodium molybdate (MoNa_2O_4) was purchased from Bide pharm, Shanghai, China. Humic acid was purchased from Yuanye Technology Co., Ltd., Shanghai, China.

2.2. Soil Samples

Surface soil samples (0–20 cm depth) were collected from the metasequoia forest at Nanjing University of Science and Technology, China. The soil exhibited a moisture content of 12.79%, pH of 8.56, conductivity of $0.031 \pm 0.004 \mu\text{S}/\text{cm}$, and redox potential of $244.6 \pm 31 \text{ mV}$. Fresh surface soil was manually cleared of debris and organic residues (plant/animal matter), dried in a desiccator for 48 h, and homogenized by grinding to pass through a 0.9 mm sieve. The dielectric constant of dried soil was measured to be 3.01 (imaginary part 0.05). The mineral characteristics of soil are presented in Table A1, Appendix A. A pyrene–acetonitrile stock solution (10,000 mg/L) was prepared by dissolving a measured amount of pyrene in acetonitrile. For soil spiking, 2 mL of the stock solution was added to 70 mL of dichloromethane, mixed thoroughly with 200 g of dried soil, and left in a fume hood for 24 h to ensure complete evaporation of the dichloromethane. This process resulted in pyrene-contaminated soil with a final concentration of 100 $\mu\text{g}/\text{g}$.

2.3. Experimental Procedure

In this study, three experiments were conducted, namely, Experiment I, II, and III. All the experiments were performed in duplicate.

Experiment I aimed to investigate the performance of the MW/PS system in degrading pyrene. The experiment was conducted using a laboratory microwave reactor (MKJ-J1N, Maiiway Microwave Co., Ltd., Qingdao, China), operating at a frequency of 2.45 GHz with adjustable power (0–800 W) and programmable temperature/time control (Figure A1,

Appendix B). The frequency of 2.45 GHz is common in commercial microwave facilities, and it can avoid possible interference with other radio waves. For each trial, 10 g of dried soil (containing 100 µg/g pyrene) was weighed into an evaporating dish, followed by the addition of 1 mL persulfate solution ($\text{Na}_2\text{S}_2\text{O}_8$, 0.5, 1, and 2 M; equivalent to 11.9, 23.8, and 47.6 mg/g in soil). The mixture was homogenized with a glass rod, immediately transferred to the microwave reactor, and monitored using a temperature sensor in real time. Microwave power (200–600 W), different temperatures (40, 60, and 80 °C), and different reaction durations (2–30 min) were set during the experiment. Notably, the temperature was regulated at the set values via intermittent microwave cycling (on/off). Upon reaching the preset reaction time, the soil was collected for pyrene extraction and analysis. Additionally, to investigate the effect of different soil factors, the degradation of pyrene in the MW/PS system (80 °C and 23.8 mg/g persulfate) was assessed using differently prepared soils with different contamination levels (50–200 µg/g pyrene), moisture contents (10–30%), and humic acid concentrations (0–3% humic acid).

Experiment II aimed to investigate the performance of the thermal-activated persulfate (TH/PS) system in degrading pyrene. This system utilized a constant-temperature water bath (LC-WB-1, Lichen Technology Co., Ltd., Shanghai, China) as the heat source, with experimental procedures similar to the MW/PS system, except for two modifications: (1) a round-bottomed flask replaced the evaporating dish as the reaction vessel, and (2) the flask was submerged in a preheated water bath (40 °C, 60 °C, or 80 °C) for the specified duration (2–30 min). In this experiment, the water bath heating only increases the temperature via heat exchange, which differs from the combined effects of molecular vibration and localized heating in the WM/PS system. Therefore, the PAH degradation resulting from molecular vibration can be distinguished by comparing these two systems.

Experiment III aimed to investigate the role of different ROS in the MW/PS system. To identify the specific ROS, several selective quenching agents, pre-mixed with the persulfate solution, were introduced prior to the MW/PS treatment: MeOH for $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, TBA for $\bullet\text{OH}$, BQ for $\text{O}_2^{\bullet-}$, and DABCO for $^1\text{O}_2$ [5,26,27]. All other experimental steps followed the standard MW/PS protocol. To further evaluate the role of $^1\text{O}_2$, additional experiments were conducted using H_2O_2 and MoNa_2O_4 combinations to generate $^1\text{O}_2$ for pyrene oxidation, without the addition of persulfate. A 1:1 (v/v) mixture of deionized water and acetonitrile (50 mL) was prepared as the reaction solution, spiked with 0.1 mL of a 1000 mg/L pyrene–acetonitrile stock solution. Three experimental conditions were tested: (1) 0.1 mL H_2O_2 , (2) 1.15 g MoNa_2O_4 , and (3) 0.1 mL H_2O_2 + 1.15 g MoNa_2O_4 . Each mixture was stirred thoroughly, reacted for 30 min, and analyzed for pyrene concentration changes to assess $^1\text{O}_2$ -driven degradation.

2.4. Analytical Methods

Pyrene in soil was extracted using an ultrasonic-assisted extraction method [28]. Soil samples were transferred to 50 mL beakers, and dichloromethane was added as the extraction solvent, ensuring that the liquid level exceeded the soil surface by 2 cm. The mixture was filtered through filter paper lined with anhydrous sodium sulfate, repeated 3 times, and the filtrate was concentrated using a nitrogen evaporator. The concentrate was purified using a magnesium silicate solid-phase extraction cartridge, solvent-exchanged to acetonitrile, and transferred to a 2 mL vial. Pyrene concentration was measured using high-performance liquid chromatography (HPLC, Agilent 1200, the USA) equipped with a UV detector set at 230 nm. The separation of pyrene was performed in a C18 column using an acetonitrile–water mobile phase (60:40, v/v) flowing at 1.0 mL/min. The overall extraction efficiency of this method was higher than 85%.

The ROS were analyzed using an electron paramagnetic resonance (EPR) spectrometer [29]. After 3 min of oxidation treatment, the soil was collected from the reactor. For detection, 0.1 g of soil was combined with 300 μ L of 0.1 M spin trap agent, including DMOP-H₂O (for capturing $\bullet$ OH and $\text{SO}_4^{\bullet-}$), DMPO-MeOH (for capturing $\text{O}_2^{\bullet-}$), and TEMP-MeOH (for capturing $^1\text{O}_2$) [30]. The mixture was vortexed for 1 min, filtered through a 0.45 μ m membrane, and loaded into a capillary tube sealed with vacuum grease. The capillary was secured in an EPR tube and analyzed at room temperature under the following conditions: center field 3500 G, microwave power 6.325 mW, magnetic field scan width 200 G, time constant 15 ms, scan time 30.0 s, and 5 cumulative scans.

X-ray photoelectron spectroscopy (XPS) was employed to detect changes in the valence states of specific metals before and after soil treatment. X-ray fluorescence (XRF) spectroscopy was used to analyze the minerals and metal oxides in the soil. The conductivity and redox potential were measured using a conductivity electrode (Leici DJS-1C, Shanghai, China) and a redox electrode (Leici 501OPR, Shanghai, China), respectively. The dielectric constant of the soils with 0% and 20% moisture content was determined at 2.45 GHz using a vector network analyzer (Keysight PNA-N5244A, the USA). The degradation intermediates were analyzed using gas chromatography–mass spectrometry (GC-MS, Agilent 7890B-5977, the USA) equipped with an Elite-5 capillary column (30 m $\times$ 0.25 mm i.d., 0.25 μ m df). The soil sample was collected from the MW/PS reactor after a 5-min reaction and then subjected to an extraction procedure identical to that used for HPLC measurements. The column was operated in temperature-programmed mode: initially set at 35 $^\circ\text{C}$ for 2 min, then increased at 10 $^\circ\text{C}/\text{min}$ to 150 $^\circ\text{C}$, maintained at 150 $^\circ\text{C}$ for 5 min, further increased at 3 $^\circ\text{C}/\text{min}$ to 290 $^\circ\text{C}$, and maintained at 290 $^\circ\text{C}$ for 2 min. The inlet temperature was set to 280 $^\circ\text{C}$, and the scanning mass range was 35–450 m/z. Based on previous studies, the toxicity and bioaccumulation factor of the generated intermediates were evaluated using the Toxicity Estimation Software Tool (T.E.S.T., Version 5.1.2) [5].

3. Results and Discussion

3.1. MW/PS Performance Under Different Operational Conditions

Experiments were conducted at different temperatures and persulfate concentrations to assess the performance of the MW/PS system and the operational factors influencing pyrene degradation. Figure 1a illustrates the degradation of pyrene at different magnetron powers. The soil temperature in all groups can reach the set values within 1 min (Figure A2, Appendix B), allowing the initial heating process to be considered negligible. Increasing the power from 200 W to 400 W increased the degradation efficiency, while further increasing to 600 W had minimal effect. Hence, 400 W was chosen as the operational power for the subsequent experiments. Figure 1b illustrates the degradation of pyrene at different temperatures. At 80 $^\circ\text{C}$, the system achieved the fastest pyrene degradation, with a removal of 76.5% within the initial 10 min and a final removal of 85.3% after 30 min. The degradation process fitted the pseudo-second-order kinetics well (Table A2, Appendix A; Figure A4, Appendix B). In contrast, lower temperatures resulted in slower removal rates: 34.9% (40 $^\circ\text{C}$) and 42.7% (60 $^\circ\text{C}$) within 10 min, rising to 54.9% and 61.4%, respectively, after 30 min. This was consistent with many previous studies, which have shown that 80 $^\circ\text{C}$ is an optimal temperature for the MW/PS system [19,20,23]. While higher temperatures can lead to more intensive activation of persulfate, further increasing the temperature is not generally recommended due to concerns about cost and energy consumption.

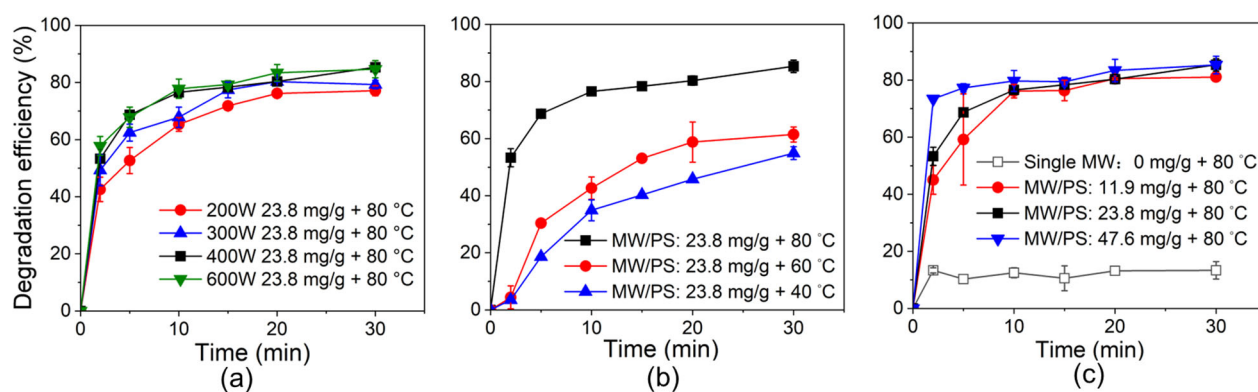


Figure 1. The degradation of pyrene in the MW/PS system conducted at different (a) powers, (b) temperatures, and (c) persulfate concentrations.

The effect of persulfate concentration was evaluated at 80 °C, as shown in Figure 1c. Without persulfate addition (single microwave treatment), pyrene removal was only 13.3% over the entire 30-min treatment period, highlighting the crucial role of persulfate in pyrene degradation. However, the addition of 11.9–47.6 mg/g persulfate significantly accelerated pyrene degradation, and the final removal efficiencies were comparable (>80%) across the different concentrations, with less than 4.3% differences. With 47.6 mg/g persulfate, 77.3% pyrene removal occurred within 5 min, while lower persulfate concentrations required 10 min to achieve similar removals. Notably, while the temperature significantly enhanced pyrene degradation, the persulfate concentration primarily affected the reaction rate rather than the final removal efficiency. Based on these findings, 23.8 mg/g persulfate and 80 °C were the optimal activation conditions, balancing rapid degradation and high removal efficiency (85.3%).

3.2. MW/PS Performance Associated with Soil Characteristics

The characteristics of contaminated soil, including the pyrene concentration, moisture content, and humic acid levels, can significantly impact the performance of the MW/PS system [16]. Figure 2a illustrates the effect of the pyrene concentration on the degradation efficiency, demonstrating that higher pyrene concentrations resulted in poorer degradation outcomes. At pyrene concentrations of 50, 100, and 200 µg/g (in soil), the final degradation rates after 30 min were 95.4%, 85.3%, and 80.9%, respectively. The addition of water from a 0% to 20% moisture content can increase the dielectric property of soil, from 3.01 (imaginary part 0.05) to 8.89 (imaginary part 2.72). Figure 2b highlights the effect of moisture on pyrene degradation, showing that the degradation rate improved as the moisture content increased. In the absence of water, the slow removal of pyrene can be attributed to the desorption of pyrene from the soil to the atmosphere, rather than chemical decomposition. At a moisture content of 10%, the final degradation rate was only 73%, while at 20% moisture content, it increased to 85.3%. The higher dielectric constant of H₂O (80), compared to dry soil (2–5), enabled the MW/PS system to capture microwave energy better, resulting in higher temperatures [31]. It is noteworthy that microwave heating caused a 54% decrease in the moisture content during the experiment, resulting in a slight decrease in the dielectric constant (Figure A3). However, it did not significantly affect pyrene degradation within the first 10 min. Additionally, the reaction between SO₄^{•−} and H₂O can generate •OH [32], which favors the splitting of S₂O₈^{2−} and rapid degradation of pyrene. However, increasing the moisture to 30% did not further enhance the degradation rate, indicating that 20% moisture was sufficient for the MW/PS system. Figure 2c presents the effect of humic acid on pyrene degradation. The results show that adding 1–2% humic acid to the soil did not significantly affect pyrene degradation. However, the degradation rate decreased when

the humic acid concentration was increased to 3%. Humic acid, a common organic matter in soils, can quench radicals involved in the advanced oxidation processes [33–35]. This competitive quenching reduced the quantity of available radicals for pyrene degradation, thereby lowering the degradation efficiency.

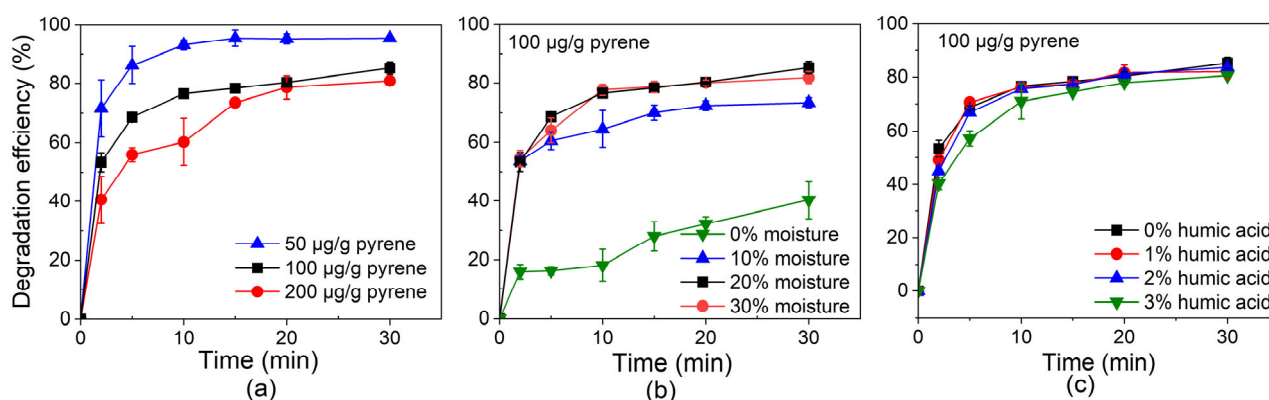


Figure 2. The degradation of pyrene with different (a) pyrene concentrations, (b) moisture levels, and (c) humic acid contents. Operational conditions: 80 °C and 23.8 mg/g persulfate.

Overall, the findings regarding the contamination levels, moisture, and humic acid content have provided valuable insights for optimizing the MW/PS system. The addition of persulfate should be based on the pyrene contamination levels in the soil to avoid chemical waste. When the soil moisture content is below 20%, increasing the moisture can enhance the degradation efficiency. In addition, the soil humification levels are an important factor that can also influence the degradation efficiency. In practice, it is essential to consider the specific characteristics of the soil to determine the optimal operational conditions and chemical dosages, thereby improving the overall cost-effectiveness.

3.3. Comparison of MW/PS and TH/PS Systems

In the MW/PS system, microwaves can theoretically activate persulfate through thermal activation and molecular vibration [36]. Figure 3 illustrates the removal of pyrene using the MW/PS and TH/PS systems, which helps to differentiate the contributions from thermal activation and molecular vibration. The MW/PS system achieved significantly higher removal efficiency up to 85.3%, indicating that microwave effectively activated the persulfate in the MW/PS system. However, the TH/PS system demonstrated only a 55.8% removal efficiency, suggesting that heating to 80 °C alone was insufficient for adequate persulfate activation. Notably, the single microwave only caused the removal of 13.3% of the pyrene, as shown in Figure 1b, indicating that molecular vibration alone was insufficient for effective pyrene degradation. Microwaves, as electromagnetic waves, can induce the vibration of dipolar molecules in the soil during irradiation [37]. The absorption of electromagnetic energy can generate heat, causing a uniform and rapid increase in temperature, which enhances the reactivity of chemical reactions in the soil [38]. In addition, as a polar substance, persulfate disperses rapidly in the soil under microwave irradiation, facilitating the generation of ROS upon contact and collision with soil particles [39]. The hotspot effect of microwaves can also enhance the decomposition of persulfate [40]. Once the microwave is removed from the system, the heating effect persists, but molecular vibration disappears. However, the abundant ROS generated from microwave exposure remain effective in pyrene degradation for a short time. Compared to thermal activation, microwave activation demonstrated higher pyrene degradation due to the combined effects of both thermal activation and molecular vibration.

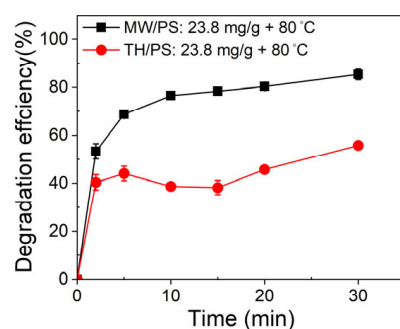


Figure 3. Removal of pyrene using single microwave, TH/PS, and MW/PS systems.

3.4. ROS Generated During Activation

To clarify the differences between thermal activation and molecular vibration effects during oxidation, EPR was employed to detect and compare the ROS generated in both the MW/PS and TH/PS systems. Figure 4a presents the EPR results for the MW/PS system using DMPO-H₂O as the scavenger, which show distinct signals corresponding to $\bullet\text{OH}$, with a 1:2:2:1 intensity pattern, and $\text{SO}_4^{\bullet-}$, with a 1:1:1:1:1 intensity pattern [41]. These signals were strengthened with the increase in temperature, indicating the temperature-dependent formation of radicals. In general, the soil pH can significantly influence the generation and stability of $\text{SO}_4^{\bullet-}$ in the persulfate-based oxidation system. In this study, the relatively high soil pH (8.56) facilitated the conversion of $\text{SO}_4^{\bullet-}$ into $\bullet\text{OH}$ [42]. This explains the concurrent detection of both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ in the MW/PS system. The use of DMPO-MeOH as the scavenger did not yield any noticeable peaks (Figure 4b), suggesting that $\text{O}_2^{\bullet-}$ was either not generated or present at very low concentrations in this system. However, signals consistent with a 1:1:1 intensity, indicative of $^1\text{O}_2$, were detected in this system (Figure 4c). Importantly, no significant change in the peak intensities of $^1\text{O}_2$ was observed with temperature variation, suggesting that its formation was likely related to microwave activation. This is consistent with previous findings on the degradation of chlorpyrifos using MW/PS system, where $^1\text{O}_2$ was found during oxidation [43]. These results imply that both radical ($\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$) and non-radical ($^1\text{O}_2$) pathways may be involved in the MW/PS system.

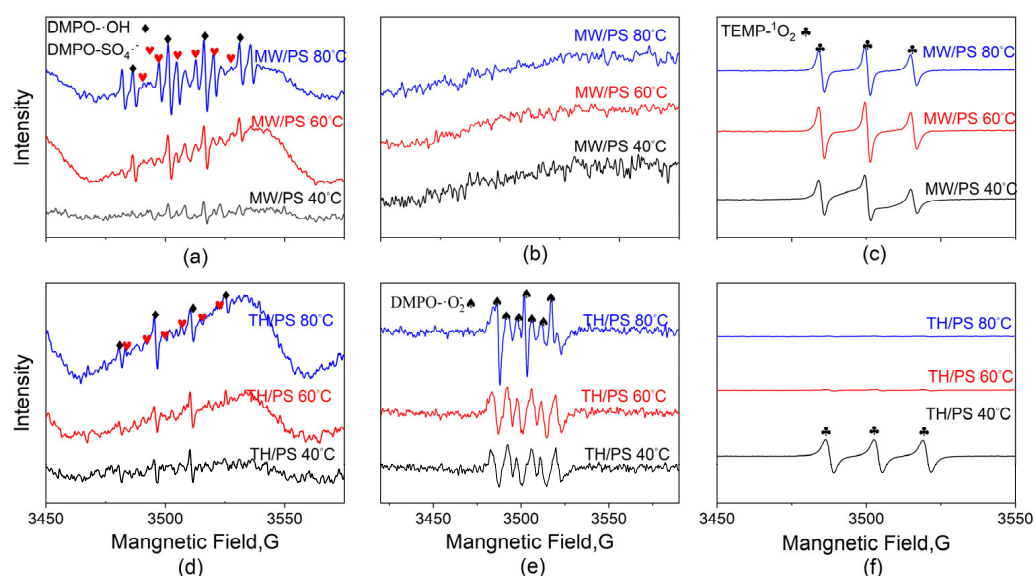


Figure 4. EPR detection results of the MW/PS system using (a) DMPO-H₂O, (b) DMPO-MeOH, and (c) TEMP-MeOH combinations; and the TH/PS system using (d) DMPO-H₂O, (e) DMPO-MeOH, and (f) TEMP-MeOH combinations.

As shown in Figure 4d, the TH/PS system also produced $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$. However, their peak intensities were lower than those observed in the MW/PS system, consistent with the slower pyrene degradation in the TH/PS system. It is noteworthy that signals of 1:1:1:1:1 intensity indicating $\text{O}_2^{\bullet-}$ were detected (Figure 4e), which differed from the results in the MW/PS system. While $^1\text{O}_2$ was also detected in the TH/PS system, its peak intensities decreased significantly as the temperature increased (Figure 4f), raising questions about its role in this system. This can be attributed to the loss of $^1\text{O}_2$ from the soil to the atmosphere due to the increase in temperature.

3.5. ROS Validation Using Quenching Experiments

Quenching experiments using various scavengers were conducted to elucidate the relative contributions of different ROS in the degradation of pyrene in the MW/PS system. As shown in Figure 5a, the addition of 0.1 M and 1 M MeOH (pre-mixed with persulfate solution) reduced pyrene degradation by approximately 21.6% and 38.9%, respectively, within the first 2 min. This indicated that both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ played important roles in this system. Similarly, as shown in Figure 5b, the degradation of pyrene was weakened with the addition of TBA to quench $\bullet\text{OH}$. However, within the first 2 min, this decrease was only 15.0% and 20.9% for 0.1 M and 1 M TBA, respectively, lower than using MeOH as the scavenger. This suggests that $\text{SO}_4^{\bullet-}$ alone partially contributed to the pyrene degradation. Interestingly, the quenching effect in the above experiments diminished over time, achieving similar removal efficiencies after 15 min, likely due to the gradual evaporation of MeOH as the temperature increased.

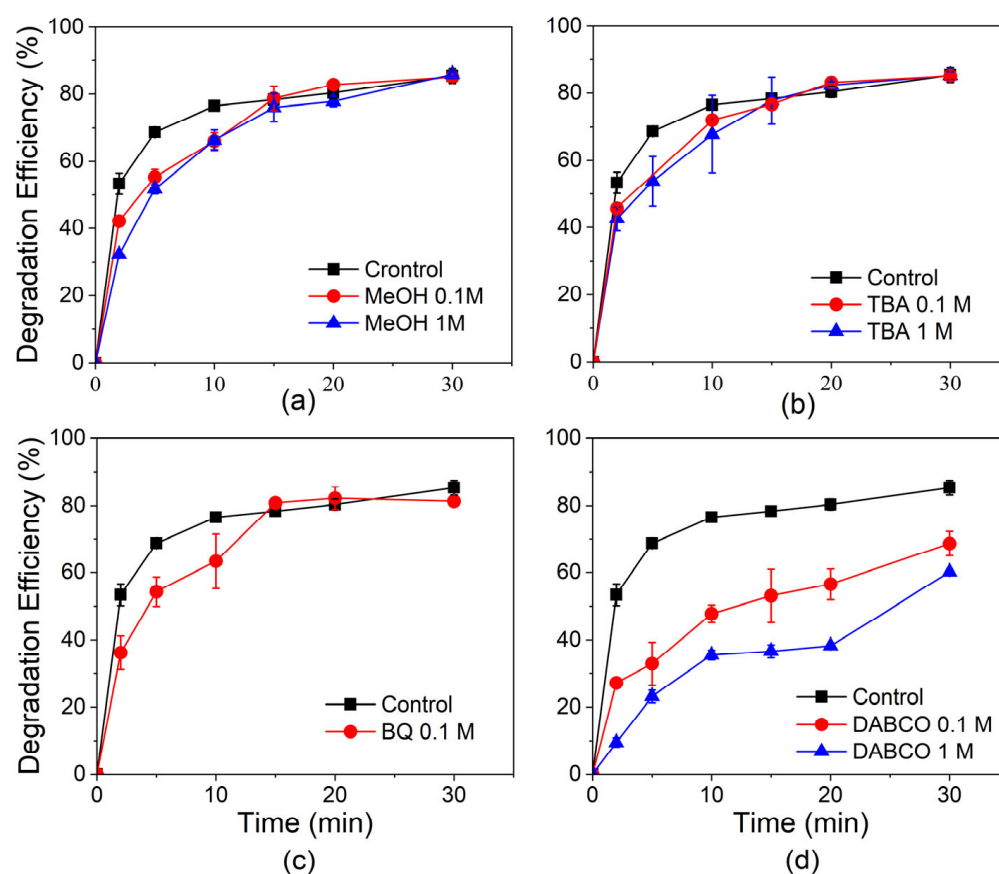


Figure 5. Quenching results for the MW/PS system after adding (a) MeOH, (b) TBA, (c) BQ, and (d) DABCO as scavengers. Note: 1 M BQ was not fully dissolved in water.

According to the EPR results, $O_2^{\bullet-}$ was not detected in the MW/PS system. However, in the quenching experiment, the degradation of pyrene was hindered by approximately 17.5% with the addition of 0.1 M BQ, as shown in Figure 5c. This suggests that the inhibitory effect of BQ was not due to the quenching of $O_2^{\bullet-}$. Previous studies have shown that BQ can compete with persulfate for electrons and be reduced to form 4-hydroquinone [44], which impedes persulfate activation and consequently reduces pollutant removal rates. In Figure 5d, the addition of 0.1 M and 1 M DABCO decreased pyrene degradation by approximately 17.0% and 25.0%, respectively, indicating that $^1O_2$ may play a significant role in the oxidation process. However, some studies have found that $^1O_2$ readily undergoes electrophilic addition reactions with unsaturated organic compounds [45]. Other research has observed that, when reacting with PAHs, $^1O_2$ adds to two opposite carbon atoms on the benzene ring but does not cleave them into smaller molecules [46]. These findings are inconsistent with the quenching results in this study, suggesting that further experiments are required to investigate the role of $^1O_2$ in the MW/PS system.

Figure 6a shows the changes in the pyrene concentration in the additional experiments using H_2O_2 , $MoNa_2O_4$, and $H_2O_2 + MoNa_2O_4$ as $^1O_2$ generators. It is evident that the addition of these substances did not lead to pyrene degradation, as approximately 21.5 mg/L of pyrene was detected after 30 min of reaction in all of the experimental groups. This suggests that no degradation of pyrene occurred in these systems. However, as shown in Figure 6b, a 1:1:1 peak pattern corresponding to $^1O_2$ was detected, indicating that $^1O_2$ cannot directly oxidize pyrene, despite being sufficiently provided. Therefore, it is inferred that the decrease in pyrene degradation observed in Figure 5d was due to the competitive effect caused by DABCO addition. Previous studies have reported $^1O_2$ generation in the MW/PS system [5,21]. In these studies, combined with the quenching results, it was concluded that $^1O_2$ played a role in pyrene degradation. However, most recent studies have suggested that the role of $^1O_2$ might be overestimated, as the used quenchers can also react with persulfate and radicals [47,48]. The results of this study support this perspective, showing that, although $^1O_2$ can be generated, its contribution to pyrene degradation was negligible. Nonetheless, the possibility that $^1O_2$ may interact with certain degradation intermediates cannot be ruled out.

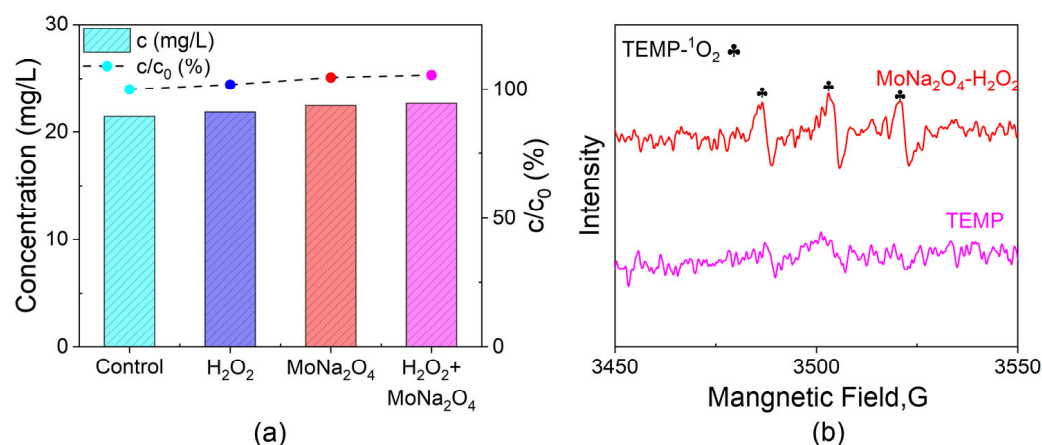


Figure 6. (a) Concentration of pyrene before and after the experiment using different H_2O_2 and $MoNa_2O_4$ combinations; (b) EPR results for the $H_2O_2 + MoNa_2O_4$ system.

3.6. Oxidation Mechanisms and Degradation Pathways

Based on the EPR spectroscopy, quenching experiments, and XPS analysis results, the roles of different ROS played during oxidation can be inferred. In the TH/PS system, $S_2O_8^{2-}$ decomposed under thermal activation to generate $SO_4^{\bullet-}$, and $SO_4^{\bullet-}$ can further react with H_2O to produce $\bullet OH$. However, in the MW/PS system, the generation of

$\text{SO}_4^{\bullet-}$ was significantly enhanced due to both thermal activation and molecular vibrations, resulting in faster pyrene degradation than that in the TH/PS system. $\text{O}_2^{\bullet-}$ may be generated from the reaction between $\text{S}_2\text{O}_8^{2-}$ and H_2O [49], while it was not detected in the MW/PS system, suggesting that the generation pathways of $\text{O}_2^{\bullet-}$ differ between these two systems. $^1\text{O}_2$ was found to contribute negligibly to pyrene degradation, suggesting its limited role in aromatic ring cleavage.

Soil minerals, particularly iron (Fe) and manganese (Mn), can play significant roles in the persulfate-based oxidation system. Fe^0 and Fe^{2+} are commonly used as activators in persulfate processes, while Mn oxides have also been shown to facilitate the generation of ROS [49,50]. In this study, only Fe_2O_3 was detected in the soil, as shown in Table A1, Appendix A. This is consistent with expectations, as the sample was collected from surface soil, where Fe^{3+} is readily formed in the presence of air and rainwater. Fe^{3+} is generally unfavorable for persulfate oxidation due to its limited reactivity and the need for additional reductants to convert it into Fe^{2+} . As shown in Figure 7, the XPS analysis further confirmed the presence of Fe^{3+} , with two distinct peaks corresponding to Fe 2p_{3/2} and Fe 2p_{1/2} [46]. Notably, higher Fe^{3+} peak intensities were observed after both the MW/PS and TH/PS treatments, suggesting that certain other Fe species, but possibly below the detection limit, were oxidized to Fe^{3+} . In addition, no characteristic peaks were detected in the Mn 2p spectra, likely due to the low Mn concentration in the soil. These results indicate that the mineral composition of the soil did not significantly change during the MW/PS process. Nonetheless, the introduction of Fe^0 , Fe_3O_4 , and many Mn oxides, promising approaches to facilitate the generation of radicals, can be introduced to enhance the pyrene degradation in the soil further.

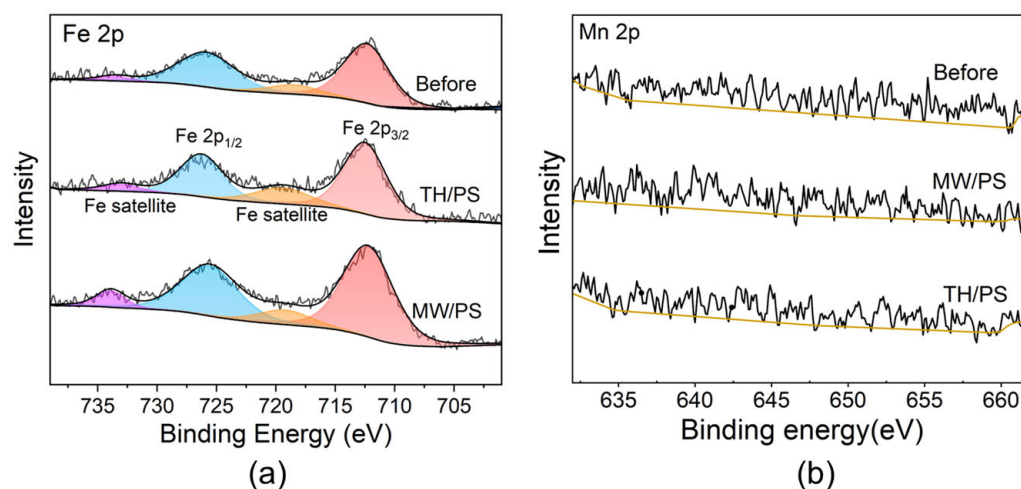


Figure 7. XPS analysis of the (a) Fe 2p and (b) Mn 2p for the soil before and after oxidation.

It is important to note that pyrene was not completely removed in the MW/PS system, suggesting that certain intermediate products may have been generated during oxidation. This study identified seven intermediate products in the 5-min reaction sample (Table A3, Appendix A, and Figure A5, Appendix B), while they were all below the detection limit after the 30-min reaction. The proposed degradation pathways of pyrene in the MW/PS system are illustrated in Figure 8. In this degradation process, the generated $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ played key roles in ring cleavage. Phenanthrene was detected in the system, while naphthalene was below the detection limit, which is similar to the findings of previous reports [21,51,52]. Phthalic acid and 4-hydroxybenzaldehyde are also common products found during pyrene degradation [5,21,51]. Finally, these products can be further mineralized into smaller organics or even into CO_2 and H_2O . The toxicities of pyrene and these products (LD_{50}) to the *Fathead minnow*, *Daphnia magna*, and *Oral rat* were assessed using

the T.E.S.T. method, as shown in Figure A6, Appendix B. The results showed that most of the intermediate products had relatively low toxicity. However, phenanthrene exhibited a higher bioaccumulation factor, which warrants closer attention. In practice, the operation of the MW/PS system should ensure the rapid degradation of phenanthrene into smaller and less toxic compounds, which can benefit both the bioavailability of contaminated soil and cost-effectiveness.

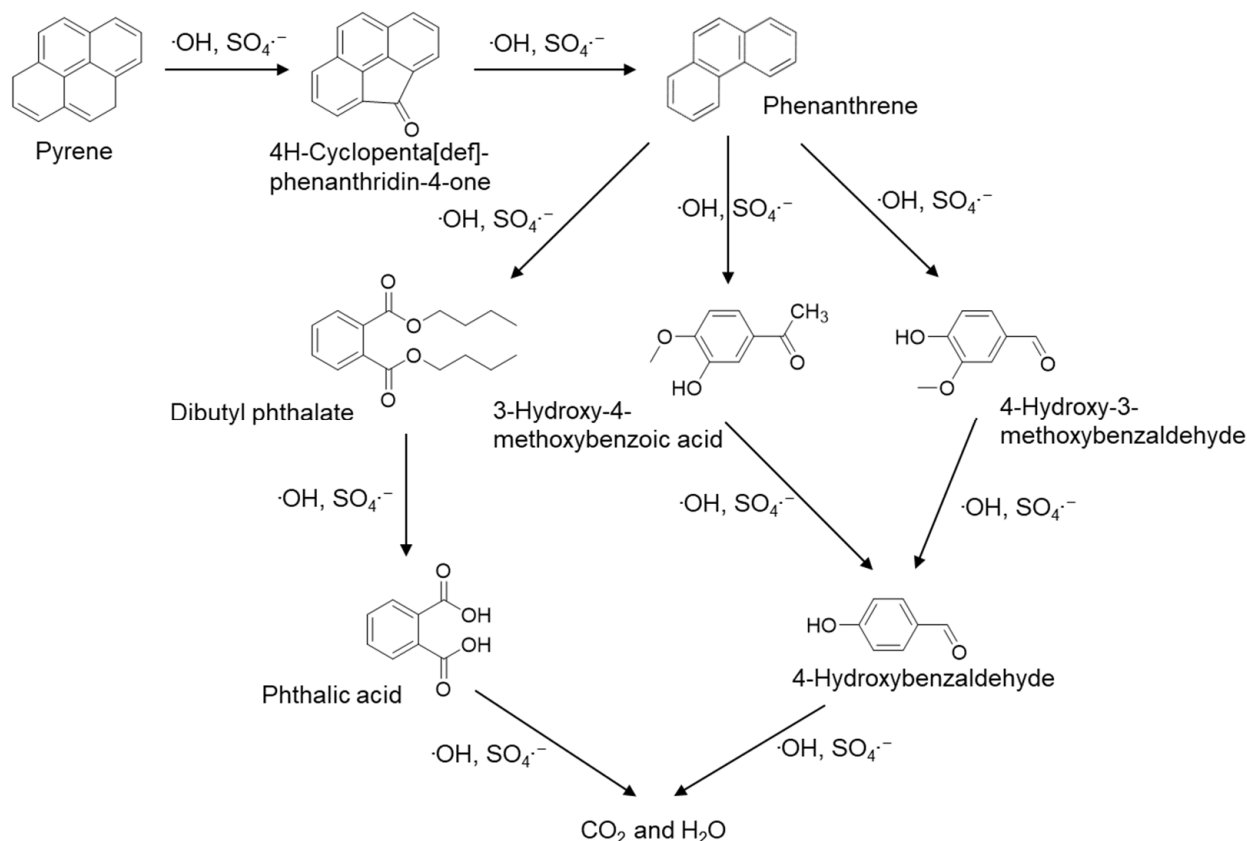


Figure 8. Possible pathways of pyrene degradation in the MW/PS system.

4. Conclusions

This study investigated the removal of pyrene using the MW/PS system and systematically analyzed the mechanisms underlying the enhanced removal efficiency. The results showed that, under 400 W, 80 °C, and 23.8 mg/g persulfate conditions, the MW/PS system contributed 85.3% removal of pyrene from the soil, which was far higher than those in the single microwave and TH/PS systems. This indicated that both thermal activation and molecular vibration play important roles in activating persulfate. In addition, increasing the temperature and persulfate concentration can enhance the degradation efficiency. The pyrene concentration, moisture, and humic acid content also influenced the degradation efficiency significantly. The EPR analysis and quenching experiments showed that $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and $^1\text{O}_2$ were generated in the MW/PS system, while only $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ were the primary causes of rapid pyrene degradation. In the MW/PS system, $\text{O}_2^{\cdot-}$ was not detected, while $^1\text{O}_2$ was generated at very high levels. However, additional experiments suggested that $^1\text{O}_2$ had no significant impact on pyrene degradation. The XPS results suggested that the MW/PS process did not change the mineral composition of soil significantly, with no significant changes observed in Fe species. Most of the generated intermediates were found to have a low toxicity and bioaccumulation potential. Overall, this study is of high instructive significance in remediating PAH-contaminated soil using the MW/PS system. Although PAHs cannot be completely degraded, applying the MW/PS system

can rapidly reduce the total PAH concentration and increase the bioavailability of the contaminated soil. Notably, adding persulfate to soil inevitably introduces sulfate into the soil, which is a major disadvantage. Therefore, the persulfate dosage should be optimized within an acceptable range that balances efficiency and environmental impact. Integrating persulfate oxidation with biological methods may improve the overall treatment efficiency in practice. Key trade-offs between persulfate dosage and bioavailability should be further investigated. Additionally, while effective activation has been observed under 2.45 GHz microwave irradiation, studies on the effects of other frequencies would be valuable for advancing the MW/PS system.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: Author Yuanming Guo, Chenglin Hou, Hongrui Li, and Wenhao Chen were employed by the company Norendar International Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Appendix A

Table A1. Mineral composition of the soil.

Components	Content (%)	Components	Content (%)
Na ₂ O	0.978	MnO	0.233
MgO	1.122	Fe ₂ O ₂	14.929
Al ₂ O ₃	11.286	ZnO	0.096
SiO ₂	53.300	Rb ₂ O	0.068
P ₂ O ₅	0.244	SrO	0.089
SO ₃	0.141	ZrO ₂	0.164
K ₂ O	2.329	BaO	0.127
CaO	1.811	PbO	0.052
TiO ₂	1.459	L.O.I.	11.57

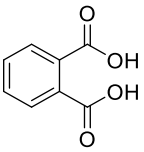
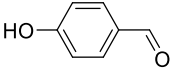
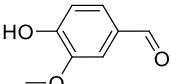
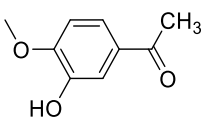
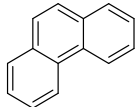
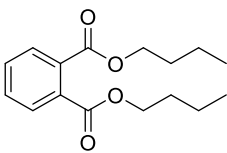
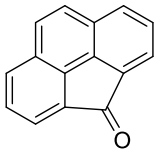
Table A2. Kinetic fitting results for the removal of pyrene under different conditions.

Experiment	Conditions	Pseudo-First-Order Model			Pseudo-Second-Order Model		
		q_e ($\mu\text{g/g}$)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($\text{mg/g}\cdot\text{min}$)	R^2
Power	200 W	73.2138	0.3243	0.9613	82.1934	0.0055	0.9894
	300 W	79.2942	0.2699	0.9219	83.3949	0.0079	0.9908
	400 W	79.8311	0.4588	0.9826	86.5131	0.0091	0.9980
	600 W	84.6555	0.4004	0.9533	86.4155	0.0106	0.9959

Table A2. Cont.

Experiment	Conditions	Pseudo-First-Order Model			Pseudo-Second-Order Model		
		q_e ($\mu\text{g/g}$)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($\text{mg/g}\cdot\text{min}$)	R^2
Temperature	80 °C	79.6741	0.5035	0.9844	86.5125	0.0091	0.9980
	60 °C	65.6981	0.1054	0.9745	89.0150	0.0010	0.9655
	40 °C	62.1284	0.0704	0.9993	89.7173	0.0006	0.9822
Persulfate	11.9 mg/g	81.1028	1.1611	0.9913	83.3576	0.0400	0.9960
	23.9 mg/g	79.6741	0.5035	0.9844	86.5125	0.0091	0.9980
	47.6 mg/g	78.6616	0.3516	0.9825	87.5311	0.0058	0.9941
Initial concentration	50 $\mu\text{g/g}$	46.9870	0.6853	0.9951	49.5859	0.0134	0.9994
	100 $\mu\text{g/g}$	76.6741	0.5035	0.9844	86.5125	0.0091	0.9980
	200 $\mu\text{g/g}$	150.306	0.2941	0.9451	173.351	0.0045	0.9794

Table A3. Intermediate products of microwave-activated persulfate degradation of pyrene in soil.

No.	Intermediates	Chemical Structure
1	Phthalic acid	
2	<i>p</i> -Hydroxybenzaldehyde	
3	4-Hydroxy-3-methoxybenzaldehyde	
4	3-Hydroxy-4-methoxybenzoic acid	
5	Phenanthrene	
6	Dibutyl phthalate	
7	4H-Cyclopenta[def]-phenanthridin-4-one	

Appendix B

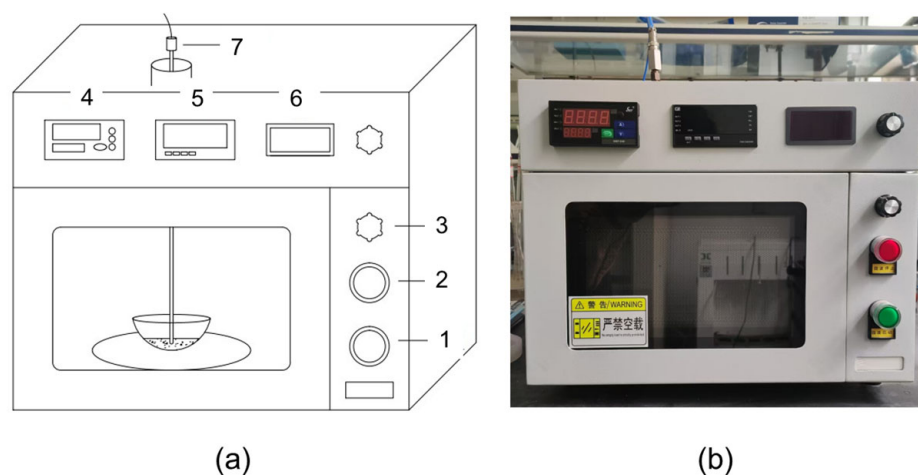


Figure A1. Schematics (a) and photograph (b) of the MW/PS system established in this study. Note: 1, start button; 2, stop button; 3, rotary knob for power adjustment; 4, temperature panel; 5, time panel; 6, power panel; 7, temperature sensor.

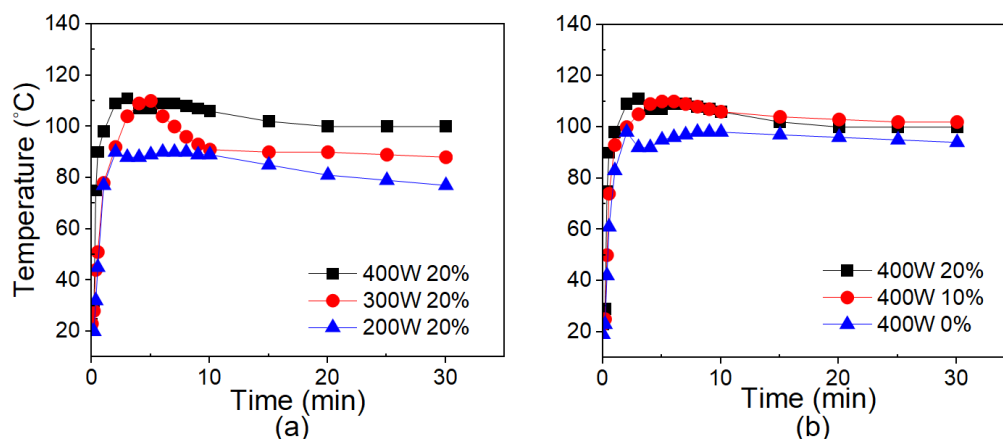


Figure A2. The increase in temperature under continuous microwave irradiation with different (a) powers and (b) moisture contents.

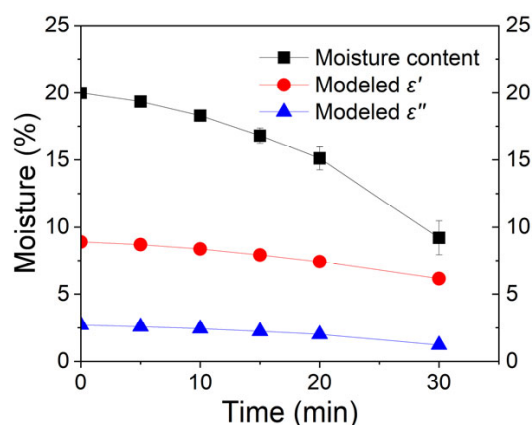


Figure A3. Moisture content and modeled dielectric constants under 400 W microwave irradiation (set at 80 °C). Note: the dielectric constants of soil with 0% and 20% moisture content were measured, while those with other moisture contents were calculated based on a previous study [53].

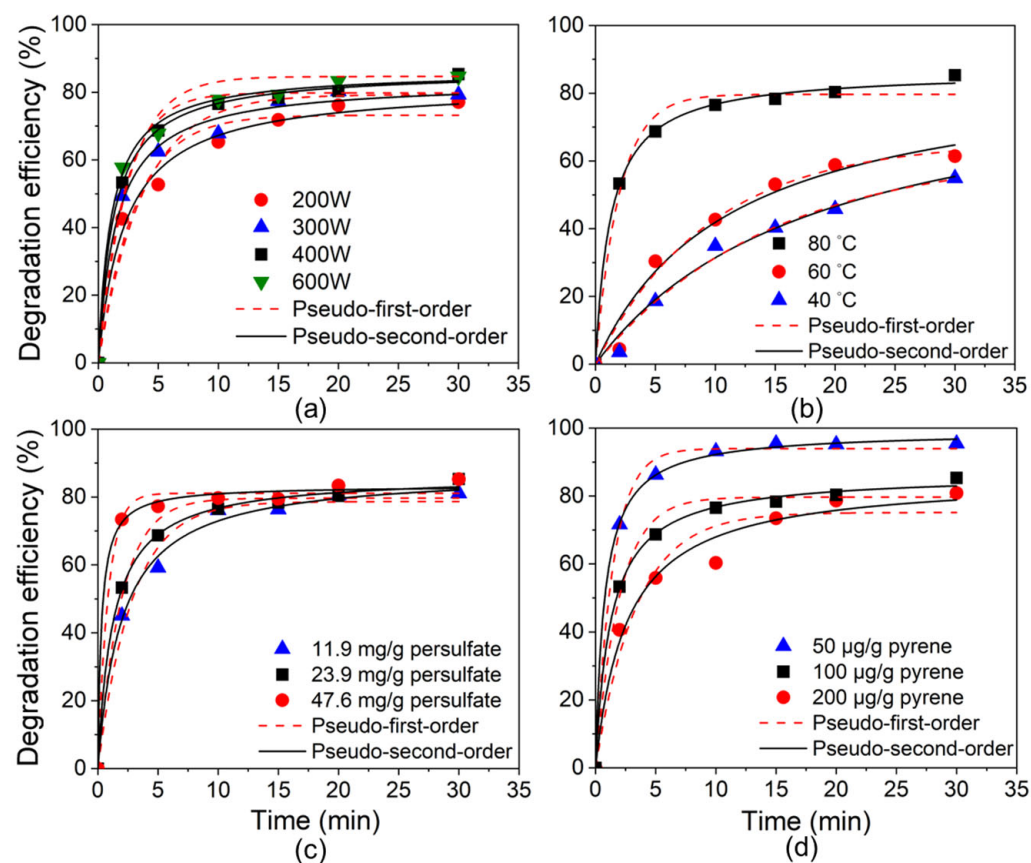


Figure A4. Fitting using pseudo-first-order and pseudo-second-order models for the experiment under (a) different powers, (b) temperatures, (c) persulfate concentrations, and (d) pyrene concentrations.

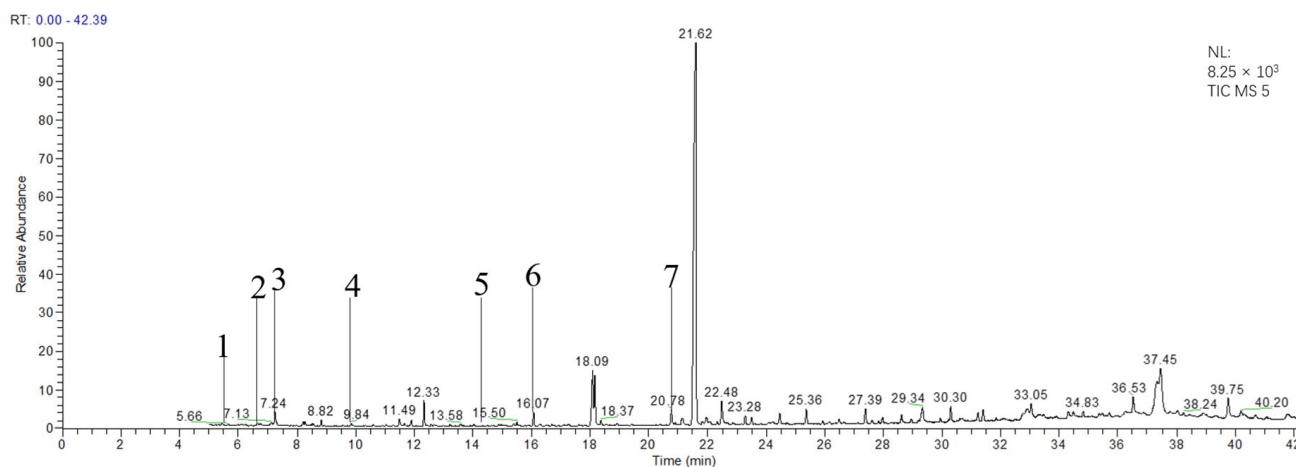


Figure A5. GC-MS spectrum of the extraction sample after the MW/PS treatment. The numbers 1–7 refer to the products marked in Table A3.

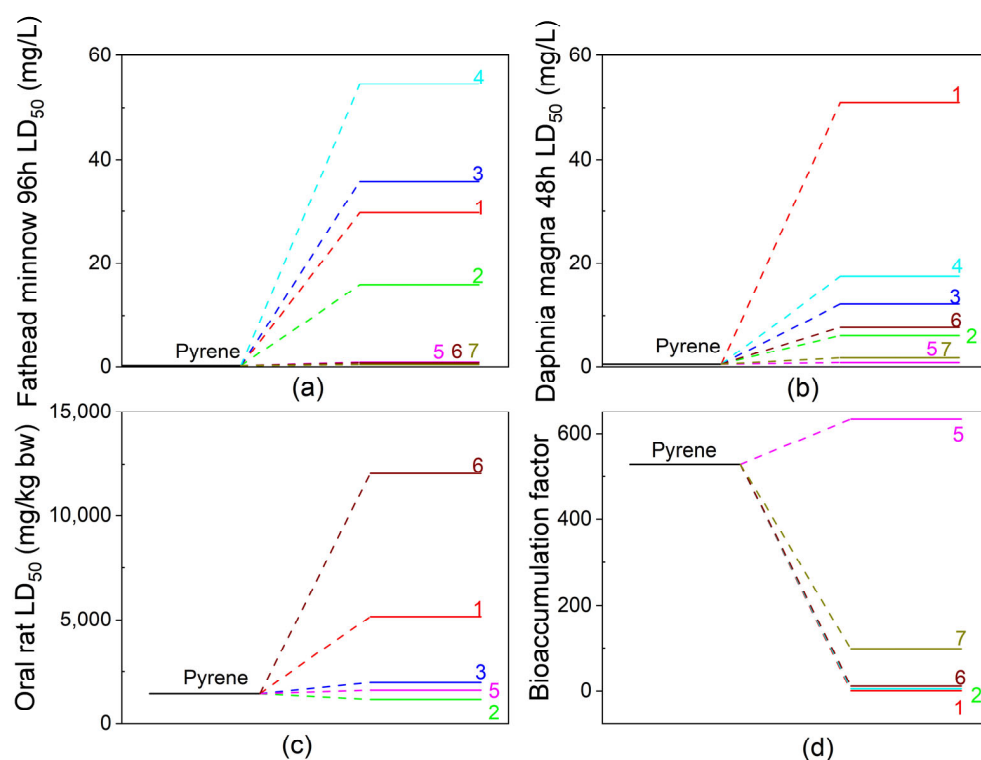


Figure A6. Toxicities to the (a) *Fathead minnow*, (b) *Daphnia magna*, and (c) *Oral rat*, and (d) bioaccumulation factors of the intermediate products generated in the MW/PS system. The numbers 1–7 refer to the products marked in Table A3.

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