

Reactive Oxygen Species-Mediated Mechanochemical Degradation of Phenanthrene in Soil over MnO₂

Tao Zhang

Liaoning Petrochemical University

Guizhou Gu

Liaoning Petrochemical University

Xin Wang

Liaoning Petrochemical University

Xiaona Wei

Liaoning Petrochemical University

Zheng Li

lizheng@lnpu.edu.cn

Liaoning Petrochemical University

Changfei Gao

Liaoning Petrochemical University

Research Article

Keywords: Phenanthrene, Contaminated soil, Mechanochemistry, Ball milling, Manganese dioxide, Reactive oxygen species

Posted Date: October 15th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11179148/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Reactive Oxygen Species-Mediated Mechanochemical Degradation of Phenanthrene in Soil over MnO₂

Tao Zhang[#], Guizhou Gu[#], Xin Wang, Xiaona Wei, Zheng Li^{*}, Changfei Gao^{*}

School of Environmental and Safety Engineering, Liaoning Petrochemical University,

Fushun, 113001, China

Abstract Phenanthrene (PHE) is a typical three-ring polycyclic aromatic hydrocarbon that is difficult to remove from contaminated soils. In this study, mechanochemistry was applied to remediate PHE-contaminated soil, and the degradation mechanism was investigated. The activity of milling aids followed the order MnO₂ > SiO₂ > NaOH > CaO; after 3 h of ball milling in the MnO₂ system, the PHE degradation rate reached 93.4%, significantly higher than that without a milling aid (43.1%). Mechanistically, mechanical force induced lattice distortion of MnO₂, generating low-valent manganese species and oxygen vacancies; adsorbed O₂ was reduced by one electron to O₂^{•-}, while ·OH formation was promoted, and both species dominated PHE ring opening and mineralization. When the grinding ball ratio and ball-to-material ratio were optimized to 4:6:1 and 25:1, the degradation rates reached 97.4% and 98.9%, respectively. Considering energy consumption, the recommended conditions are MnO₂ as the milling aid, a grinding ball ratio of 4:6:1, a ball-to-material ratio of 25:1, and a rotation speed of 500 rpm. PHE was mineralized through a pathway of aromatic hydrocarbon → quinone/anhydride → biphenyl dicarboxylic acid → benzoic acid → ring-opened diene acid → short-chain fatty acid. Ecotoxicity generally decreased during degradation.

Keywords: Phenanthrene; Contaminated soil; Mechanochemistry; Ball milling; Manganese dioxide; Reactive oxygen species

[#]These authors contributed equally to this work.

^{*}Corresponding author.

E-mail addresses: lizheng@lnpu.edu.cn (Z. Li)/ gcf1999@126.com (C. Gao)

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) consisting of two or more fused benzene rings that are widely distributed in the environment. Their major sources include the incomplete combustion of fossil fuels, industrial coking, vehicle exhaust emissions, waste incineration, and petroleum leakage from anthropogenic activities (Zhang et al. 2021a; Zhang et al. 2023c). It has been reported that several hundred thousand tonnes of PAHs are discharged into the environment worldwide every year. Owing to their semi-volatility, long-range transport potential, bioaccumulation, and high toxicity, PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) and the European Union. Among them, phenanthrene (PHE), a typical three-ring PAH, is widely detected in surface soils around coking plants, petroleum-contaminated sites, and areas with heavy traffic. PHE is highly hydrophobic ($\log K_{ow} \approx 4.46$) and tends to bind strongly to soil organic matter, forming stable bound residues that are difficult to remove by conventional physical or biological methods. Moreover, PHE and its metabolites are potentially carcinogenic, teratogenic, and mutagenic (Sleight et al. 2020; Wassenaar and Verbruggen 2021) and may enter the human body through the soil–plant–food chain, posing long-term threats to ecological security and public health. Therefore, the development of efficient, green, and economical remediation technologies for PHE-contaminated soils has become an urgent task in environmental science and engineering.

At present, remediation technologies for PAH-contaminated soils mainly include bioremediation, chemical oxidation, thermal desorption, solvent extraction, and electrokinetic remediation (Adhami et al. 2021; Chu et al. 2022; Sun et al. 2025; Wen et al. 2026). Bioremediation is regarded as the most promising green approach because of its low cost and environmental friendliness (Li et al. 2021b; Liang et al. 2021; Wu et al. 2020). However, it has clear limitations: high-molecular-weight PAHs with more rings exhibit lower bioavailability and slower microbial degradation rates; high PAH concentrations are markedly toxic to microorganisms and inhibit the

activity of degrading bacteria; and fluctuations in soil pH, temperature, moisture, and nutrient levels can strongly affect bioremediation efficiency, making it difficult to meet the demand for rapid site remediation. Chemical oxidation achieves rapid pollutant degradation by generating strongly oxidative free radicals (Sun et al. 2020; Zhang et al. 2023b); in practice, however, it suffers from large oxidant dosages, high reagent costs, and poor reaction selectivity, and excessive oxidants may damage soil organic matter and mineral structure, reducing soil fertility and causing secondary pollution (Ji et al. 2024). Thermal desorption removes PAHs from soil through volatilization or decomposition at elevated temperatures and offers high removal efficiency and wide applicability, but it requires high energy consumption and equipment investment, and high-temperature treatment may alter soil physicochemical properties and even generate highly toxic by-products such as dioxins (Li et al. 2025; Zhang et al. 2024d). Solvent extraction uses organic solvents to separate PAHs from soil, but the solvents themselves are toxic and volatile and pose a risk of secondary pollution, while solvent recovery and subsequent treatment are complex (Tao et al. 2020). In summary, existing remediation technologies face a common dilemma in field applications in which efficiency, cost, and environmental friendliness are difficult to reconcile; therefore, the development of a novel, efficient, and green remediation technology is urgently needed to break through this bottleneck.

Mechanochemistry (MC) uses mechanical force to directly induce physicochemical and structural transformations of pollutants, achieving their degradation and mineralization with no or only minimal chemical reagents. During ball milling, high-speed collisions among grinding media create instantaneous localized high-temperature and high-pressure zones that promote the cleavage of chemical bonds in pollutant molecules and simultaneously induce milling aids to generate highly reactive oxygen species, thereby accelerating pollutant ring opening, hydroxylation, and deep oxidation. Compared with conventional remediation technologies, mechanochemistry offers remarkable advantages, including simple operation, mild reaction conditions, minimal chemical reagent consumption, and a low risk of secondary pollution (Deng et al. 2021; Wang et al. 2025a; Yang et al. 2026;

Yuan et al. 2023).

The main factors governing the mechanochemical treatment of pollutants fall into two categories: ball milling conditions and the type of milling aid. Ball milling conditions include the rotation speed, milling time, and ball-to-material ratio, whereas milling aids can be classified as oxidants (zero-valent metals and metal hydrides), Lewis bases (e.g., CaO and Al₂O₃), transition metal oxides (MnO₂), and neutral substances (e.g., quartz sand). Previous studies have shown that inorganic milling aids such as SiO₂, CaO, and NaOH promote pollutant degradation by altering material surface properties, providing an alkaline environment, or participating in electron-transfer reactions (Fan et al. 2020; Xu et al. 2023; Zhang et al. 2021b), although their mechanisms and efficiencies differ considerably. As a transition metal oxide, MnO₂ can undergo lattice distortion under mechanical force and continuously release reactive oxygen species such as $\cdot\text{OH}$ through the Mn(IV)/Mn(III)/Mn(II) redox cycle, exhibiting excellent mechanochemical catalytic activity (Hu et al. 2025; Shen et al. 2021; Wang et al. 2022).

In this study, PHE-contaminated soil was selected as the target matrix to investigate mechanochemical remediation. The effects of key ball milling parameters—the type of milling aid, grinding ball gradation, ball-to-material ratio, and rotation speed—on PHE removal efficiency were systematically examined. In addition, the degradation pathway and mechanism of PHE under mechanochemical action and the ecotoxicity of the degradation intermediates were explored to provide a theoretical basis and technical support for the mechanochemical remediation of PAH-contaminated soil.

2 Materials and Methods

2.1 Test Soil

The test soil was collected from a hillside area behind Liaoning Petrochemical University, Liaoning Province, China (10–20 cm soil layer; 123.79281°E, 41.858641°N). The soil was air-dried, freed from stones, weeds, and other impurities,

ground, and passed through a 100-mesh sieve. The sieved soil was sealed in polyethylene bags and stored in the dark until use. The organic matter, ammonium nitrogen, nitrate nitrogen, total nitrogen, and moisture contents of the test soil were 5.91%, 2.44 mg·kg⁻¹, 7.41 mg·kg⁻¹, 1.69 g·kg⁻¹, and 2.75%, respectively.

To prepare PHE-contaminated soil, 50 mg of PHE was dissolved in 100 mL of methanol and added to 250 g of sieved soil in a conical flask. The mixture was shaken continuously in a shaking incubator for 48 h, transferred to a tray, air-dried, and stored in the dark until use.

2.2 Reagents

PHE, NaOH, CaO, SiO₂, and MnO₂ were purchased from Shanghai Macklin Biochemical Co., Ltd. Methanol and acetone were obtained from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. HPLC-grade n-hexane was supplied by Tianjin Siyou Fine Chemicals Co., Ltd. Except for n-hexane (HPLC grade), all chemicals were of analytical reagent (AR) grade. Ultrapure water was used throughout the experiments.

2.3 Ball Milling Experiments

PHE-contaminated soil was treated in a planetary ball mill (KE-04L, Guangzhou Chunzhou Technology Co., Ltd., Guangzhou, China). ZrO₂ grinding jars (100 mL) and ZrO₂ grinding balls were used. The grinding balls were of three diameters: large (15 mm), medium (8 mm), and small (3 mm).

The effects of the ball milling parameters on PHE removal efficiency were systematically investigated: the type of milling aid (SiO₂, CaO, NaOH, and MnO₂), the large/medium/small grinding ball ratio (1:1:1, 1:2:1, 2:1:1, and 4:6:1), the ball-to-material ratio (10:1, 15:1, 20:1, and 25:1), and the rotation speed (300, 400, 500, and 600 rpm). All experiments were conducted under static air.

2.4 Analytical Methods

Extraction of PHE from soil: 0.5 g of soil was weighed into a 50 mL centrifuge tube, and 20 mL of an acetone–n-hexane mixture (1:1, v/v) was added. After

ultrasonic extraction for 1 h, the suspension was centrifuged at 5000 rpm for 15 min. The supernatant was collected, concentrated to 0.5 mL using a rotary evaporator at 80 °C, filtered through a 0.22 µm membrane, and brought to a final volume of 25 mL with the acetone–n-hexane mixture (1:1, v/v). The final extract was transferred to a 2 mL autosampler vial for analysis.

The concentration of PHE in the extracts was determined by gas chromatography (Agilent 7890A/5975C, Agilent, USA). The GC operating conditions were as follows: injector temperature 280 °C; splitless injection; injection volume 1.0 µL; column flow rate 1.0 mL/min in constant-flow mode; and an oven temperature program of 80 °C (held for 2 min), ramped to 180 °C at 20 °C/min (held for 5 min), and then ramped to 290 °C at 10 °C/min (held for 5 min).

Degradation intermediates of PHE were determined by LC-MS (Thermo Fisher UltiMate 3000 HPLC, USA). The crystal structure of the soils before and after ball milling was analyzed by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). Fourier transform infrared spectroscopy (FTIR, FT-IR-660+610, Agilent, USA) was used to detect infrared absorption associated with molecular vibrational/rotational transitions, thereby analyzing chemical bonds and identifying functional groups. The carbonization degree of the soils before and after ball milling was evaluated by Raman spectroscopy (LabRAM HR Evolution, HORIBA Scientific, France). The pore structure parameters of the soil samples, including specific surface area, pore size distribution, and adsorption capacity, were evaluated using a fully automatic physical static analyzer (BET, Autosorb-IQ2-MP, Quantachrome, USA).

2.5 Toxicity Assessment

The molecular structures of PHE and its degradation intermediates were drawn using ChemDraw 20.0. Toxicological information was obtained by entering the corresponding chemical formulas into ECOSAR 2.2, a quantitative structure–activity relationship (QSAR)-based toxicity prediction program, to evaluate the acute and chronic toxicity of these compounds to three aquatic organisms: fish, daphnia, and green algae.

3 Results and Discussion

3.1 Effects of Milling Aid, Grinding Ball Ratio, Ball-to-Material Ratio, and Rotation Speed on PHE Degradation

Milling aids can adsorb onto soil particle surfaces, reduce surface energy and interparticle adhesion, and effectively inhibit particle agglomeration, thereby ensuring direct impact and shearing of the material by the grinding balls and increasing the probability of pollutant exposure to mechanochemically active sites. Meanwhile, milling aids are themselves mechanochemically reactive and readily undergo lattice distortion during ball milling, releasing abundant reactive oxygen species (ROS) that promote pollutant ring opening, hydroxylation, and complete mineralization (Lou et al. 2023; Song et al. 2023; Zhang et al. 2024c). As shown in Fig. 1(a), after 3 h of ball milling without a milling aid, the PHE degradation rate in soil was only 43.1%; with milling aids, PHE removal improved significantly, reaching 93.4% with MnO_2 and 87.9% and 75.3% with SiO_2 and NaOH , respectively, whereas CaO gave the lowest degradation efficiency (65.0%). Mechanochemical activation of persulfate has also been reported to efficiently remove PAHs from soil (Zhang et al. 2024a), and comparable PHE or PAH removals have been achieved with persulfate-based oxidation processes, such as biochar-supported nanoscale zero-valent iron (BC-nZVI)-activated persulfate combined with bioremediation (Zhang et al. 2020), persulfate oxidation coupled with microbial fortification (Li et al. 2021a; Liu et al. 2025), ferrous oxalate oxidation (Luo et al. 2021), and carbon-coated nZVI-activated persulfate for anthracene (Li et al. 2022). Other reported processes include Fe-based activated persulfate (Wang et al. 2024), activated-carbon-supported iron bimetal persulfate (Zhang et al. 2023a), permanganate oxidation enhanced by in situ fracturing (Shi et al. 2025), microwave/magnetite-activated persulfate for pyrene (Wu et al. 2022), and electrokinetically delivered persulfate (Yue et al. 2023b). However, these processes generally require longer treatment times, additional liquid oxidants, or complex equipment, whereas the MC process achieved comparable removal within 3

h using only solid milling aids.

The differences in PHE degradation can be attributed to the following factors. (1) During ball milling, cleavage of Si–O bonds generates reactive oxygen species such as $\equiv\text{Si}\cdot$, $\equiv\text{SiO}\cdot$, and $\equiv\text{SiO}_2\cdot$, along with $\cdot\text{OH}$ formed through their transformation, which effectively promote pollutant ring opening, hydroxylation, and mineralization; however, $\equiv\text{SiO}\cdot$ readily reacts with oxygen in the milling jar and with crystallization water in the soil to form inert surface silanols ($\equiv\text{Si-OH}$), so PHE could not be completely degraded within 3 h. (2) Under strongly alkaline conditions, excessive OH^- rapidly scavenges $\cdot\text{OH}$ to form $\text{O}^{\cdot-}$ ($\cdot\text{OH} + \text{OH}^- \rightarrow \text{O}^{\cdot-} + \text{H}_2\text{O}$), whose oxidizing capacity is weaker than that of $\cdot\text{OH}$, leading to a marked decrease in PHE degradation efficiency; meanwhile, NaOH can complex $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Mg^{2+} in the soil, passivating the metal ions required for catalytic oxidation and impeding electron transfer. (3) Calcium-based hydration products generated from CaO during ball milling may form an inert coating layer on the surfaces of PHE or oxidant particles (Zhang et al. 2023d; Zhang et al. 2024e), blocking contact with reactive sites and causing the degradation reaction to stagnate. (4) Under mechanical force, the MnO_2 lattice is distorted, and the reactive oxygen species released ($\cdot\text{OH}$) are not rapidly quenched by OH^- because the system pH is not excessively high; MnO_2 directly oxidizes PHE through the reduction of high-valent manganese ($\text{Mn(IV)} \rightarrow \text{Mn(III)/Mn(II)}$), promoting ring opening, degradation, and mineralization. Meanwhile, Mn(III)/Mn(II) is re-oxidized to active high-valent manganese oxides by oxygen introduced during ball milling and by mechanical energy, forming a catalytic cycle that continuously generates reactive oxygen species and enhances degradation efficiency.

Ball milling transfers energy mainly through the impact force produced by the falling or centrifugal collision of grinding balls and through the friction/shear forces generated by sliding and rolling between balls and between the balls and the jar wall. The greater the mass of the large balls, the higher the impact energy and the stronger the localized instantaneous high temperature, high pressure, and lattice defects generated. Medium balls bridge the friction between large and small balls, provide more effective collisions, generate more localized hot spots that activate

mechanochemical reactions, and induce deep lattice distortion of MnO_2 with the release of abundant reactive oxygen species. Small balls continuously generate fresh surfaces and defects in the interstitial spaces and uniformly distribute mechanical energy throughout the material, synergizing impact and shearing and markedly improving the utilization efficiency of the total input energy. As shown in Fig. 1(b), at a grinding ball ratio of 1:1:1, the PHE degradation rate in soil after 3 h of ball milling was only 72.7%; under this relatively low-impact ratio, the impact effect was weak, the energy density of the system remained low, and the comminution efficiency was therefore limited. Moreover, because of their small mass, the small balls mainly dispersed and homogenized the material, so PHE could not be effectively degraded at this ratio. When the proportions of large and medium balls were increased to 2:1:1 and 1:2:1, respectively, the PHE degradation rates reached 86.8% and 79.4%; at a grinding ball ratio of 4:6:1, the PHE degradation rate in soil reached 97.4%.

Because PHE is hydrophobic, the soil is prone to compaction and hardening during grinding. Sufficient grinding balls can break up soft agglomerates and continuously expose fresh surfaces. When the mass ratio of grinding balls to material reaches a certain level, the effective impact force between grinding balls is greatly enhanced, and the resulting collision energy effectively promotes the decomposition of the pollutant structure. As shown in Fig. 1(c), at ball-to-material ratios of 10:1 and 15:1, the PHE removal rates were only 70.0% and 74.1%, respectively; when the ball-to-material ratios were increased to 20:1 and 25:1, the PHE degradation rates increased sharply to 94.5% and 98.9%, respectively, after 3 h of ball milling.

The energy imparted to the material varies with the ball milling rotation speed. As shown in Fig. 1(d), at 300 rpm the PHE degradation rate in soil was only 53.2% and increased significantly with rotation speed, reaching 83.2% at 400 rpm. With further increases in rotation speed, the increase in the PHE degradation rate gradually slowed, reaching 95.0% and 96.2% at 500 and 600 rpm, respectively. This trend is consistent with previous mechanochemical remediation studies of chlorinated and brominated organic pollutants (Yao et al. 2023; Yi et al. 2021), in which pollutant removal was improved by increasing the rotation speed: the higher the rotation speed,

the greater the mechanical energy supplied to the material and the more readily the reaction proceeds. At rotation speeds below 500 rpm, the energy was insufficient to initiate PHE degradation effectively, resulting in a low removal rate. Therefore, when mechanochemistry is used to treat PHE-contaminated soil, the rotation speed should be higher than 500 rpm (Zhao et al. 2026).

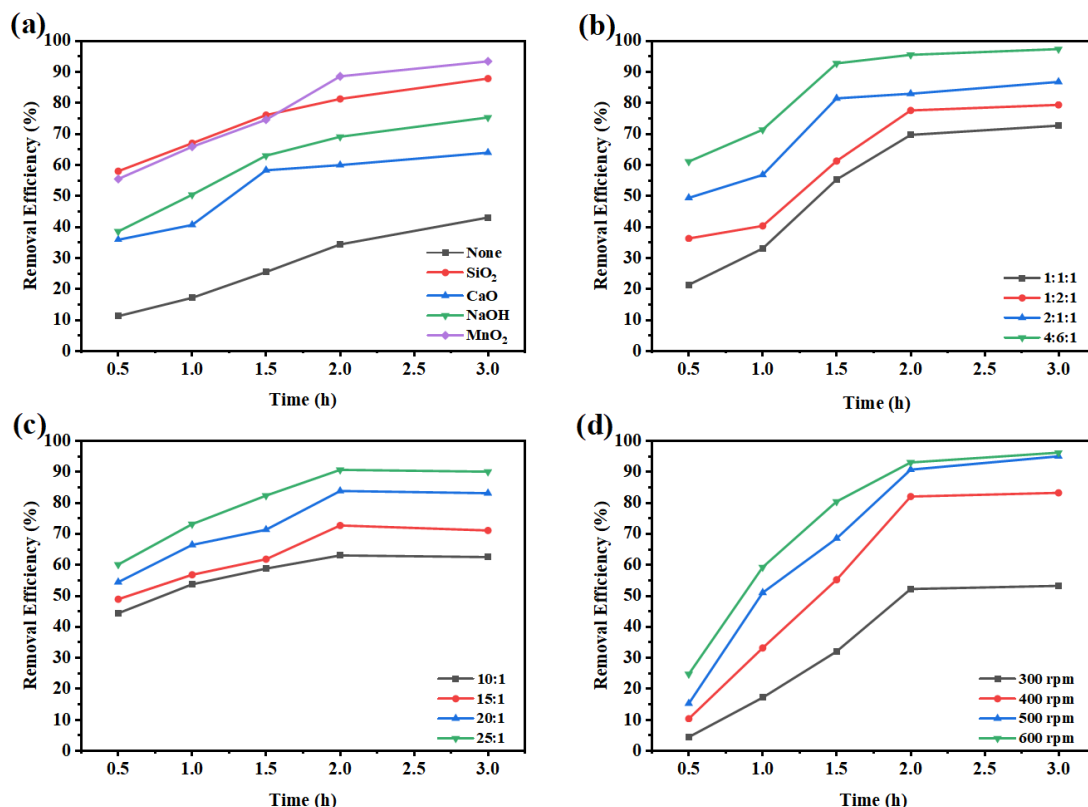


Fig. 1 Effects of (a) milling aid type, (b) grinding ball ratio, (c) ball-to-material ratio, and (d) rotation speed on PHE degradation efficiency.

3.2 Generation Pathways of Reactive Oxygen Species

Mechanical activation enhances the oxidizing capacity of MnO₂, enabling it to directly oxidize surface OH⁻ or H₂O to generate ·OH (Meng et al. 2024). Meanwhile, mechanochemistry produces localized instantaneous high temperature (>1000 K) and high pressure, which can induce the homolysis of soil pore water or of surface hydroxyl groups on MnO₂. In addition, high-speed collisions of grinding balls severely distort the MnO₂ lattice, generating oxygen vacancies and abundant low-valent manganese ions (Mn³⁺/Mn²⁺) (Chen et al. 2023; Guan et al. 2026; Wang et al. 2022). Electron-rich centers form near the oxygen vacancies, and the exposed

electron-rich sites can reduce adsorbed O_2 to $O_2^{\cdot-}$ through a one-electron reduction process (Wang et al. 2025b; Zhang et al. 2022). Meanwhile, as a p-type semiconductor, MnO_2 generates electron-hole pairs under mechanical force via the piezoelectric effect, and the electrons reduce O_2 to form $O_2^{\cdot-}$.



To gain deeper insight into the oxidative degradation mechanism of PHE in the MC system, different scavengers were added to identify the reactive species involved and the dominant ROS governing the reaction (Pan et al. 2021; Xia et al. 2025). Tert-butanol (TBA) was used as a scavenger of $\cdot OH$, while furfuryl alcohol (FFA) and benzoquinone (BQ) were used to scavenge $^1O_2$ and $O_2^{\cdot-}$, respectively (Fig. 2(a)). The addition of TBA and BQ markedly inhibited PHE removal, decreasing the degradation efficiency from 93.4% to 63.3% and 65.1%, respectively, with corresponding decreases in the degradation rate constants to 0.1390 and 0.1471 h^{-1} . In contrast, the addition of FFA had only a slight effect on PHE removal (89.7%). These results indicate that $\cdot OH$ and $O_2^{\cdot-}$ were the primary ROS responsible for PHE degradation in the MnO_2 -added MC system; their relative contributions can be ranked as $\cdot OH > O_2^{\cdot-} > ^1O_2$.

Electron paramagnetic resonance (EPR) spectroscopy was further used to analyze the possible ROS generated during PHE degradation in this system. As shown in Fig. 2(c) and (d), clear DMPO- $\cdot OH$ and BMPO- $O_2^{\cdot-}$ spin adduct signals (DMPO, 5,5-dimethyl-1-pyrroline N-oxide; BMPO, 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide) were observed, confirming the presence of abundant $\cdot OH$ and $O_2^{\cdot-}$ in the MnO_2 -added MC system. In addition, because of the low concentration and rapid transformation of $^1O_2$, its presence could not be detected by EPR (Yue et al. 2023a).

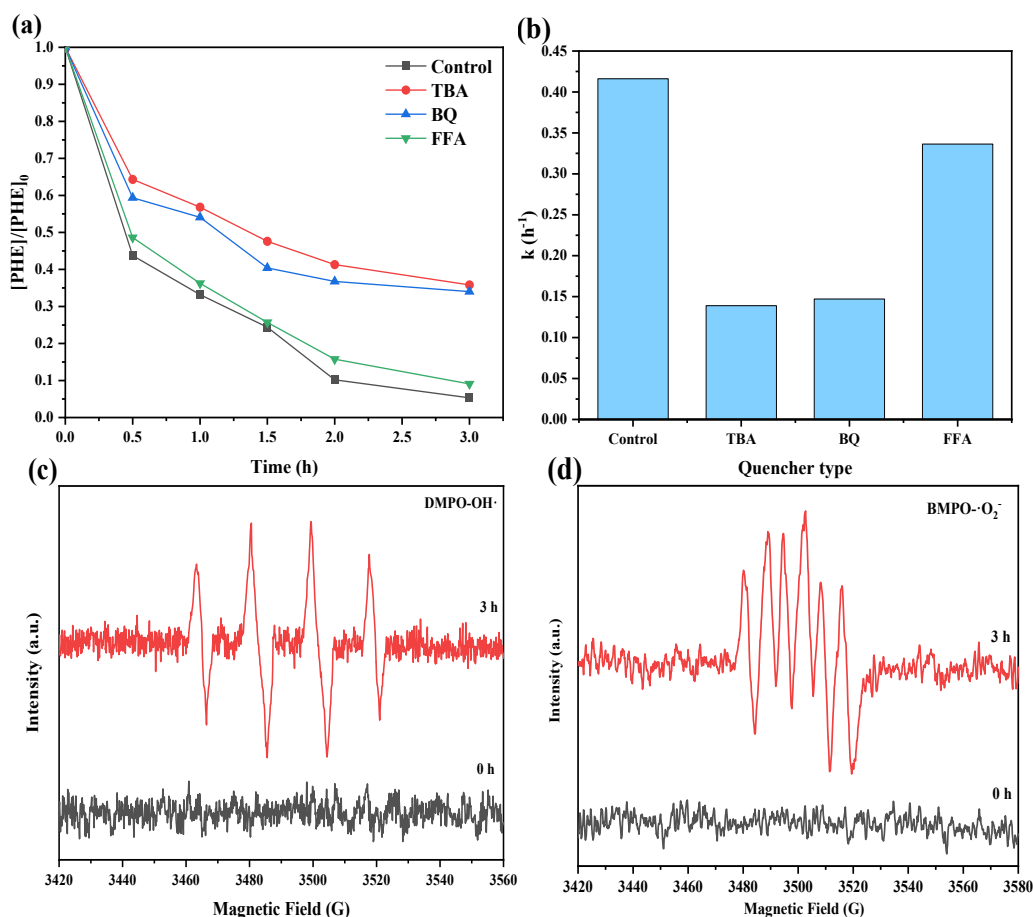


Fig. 2 (a) Effects of different scavengers on PHE degradation; (b) first-order rate constants; (c) EPR spectra of $\cdot OH$; (d) EPR spectra of $O_2^{\cdot -}$. (Conditions: $[PHE] = 0.2 \text{ mg}\cdot\text{g}^{-1}$; $MnO_2 = 0.5 \text{ g}$; rotation speed = 500 rpm; ball-to-material ratio = 25:1; grinding ball ratio = 4:6:1)

3.3 Degradation Mechanism of PHE

The SEM image of the original contaminated soil (Fig. 3(a)) showed relatively regular block-like structures with smooth surfaces and obvious layering, associated with the presence of PHE and the intact structure of the original soil; the overall structure was loose. In contrast, after MC treatment for 3 h (Fig. 3(b)), the particle morphology changed significantly: the layered structure was broken and the surface became rough and porous, forming an agglomerated porous structure. This indicates that the mechanical force during ball milling produced instantaneous high-temperature and high-pressure effects. On the one hand, these effects destroyed the crystal structures of MnO_2 and PHE, reduced the constraint between soil particles, and promoted PHE degradation and mineralization. On the other hand, they altered

the morphology of soil particles and the crystal structures of minerals, increased the specific surface area, and facilitated the exposure of more active sites, such as newly formed functional groups and unsaturated bonds generated by structural destruction, thereby enhancing the cleavage of PHE chemical bonds.

XRD patterns of PHE-contaminated soil at different ball milling times (Fig. 3(c)) showed that MC did not change the mineral composition of the soil; the main crystalline phases remained quartz (SiO_2), calcite (CaCO_3), and hematite (Fe_2O_3). However, the intensities of the (100), (101), (110), (102), (200), (201), (112), and (211) diffraction peaks gradually decreased and the peaks broadened with prolonged treatment, indicating a decline in mineral crystallinity, lattice distortion, weakening of Si-O bonds, and enhanced surface reactivity. With increasing mechanical action, soil organic matter and pollutants were eventually transformed into amorphous or graphitic carbon. The mechanochemical effect also caused particle surfaces to release energy through relaxation, forming electron-rich regions and conferring higher activity on the soil.

FTIR spectra (Fig. 3(d)) further revealed the mechanochemical evolution of the soil matrix and its surface functional groups. The original soil was dominated by the Si-O-Si asymmetric stretching band of clay and amorphous silicates at 1030 cm^{-1} , together with the characteristic quartz bands at 464 and 797 cm^{-1} . After 0.5-1 h of ball milling, the $1036\text{-}1040\text{ cm}^{-1}$ band and the quartz bands were markedly intensified, indicating that organic coatings on mineral surfaces were stripped away and that silicate structures were increasingly exposed. After 2-3 h, the $1030\text{-}1040\text{ cm}^{-1}$ band almost disappeared while the quartz band near 1090 cm^{-1} became dominant, with the ratio $I_{1090}/(I_{1030} + I_{1090})$ increasing from 0.09 to 0.94; this demonstrated that the Si-O bonds of layered and amorphous silicates were severely weakened and that the soil matrix was progressively disordered and comminuted, consistent with the decline in mineral crystallinity observed by XRD. Meanwhile, the broad O-H stretching band at $3420\text{-}3440\text{ cm}^{-1}$ continuously intensified, reflecting the formation of abundant surface hydroxyl groups and hydroxylated or carboxylated species under ROS attack, and the band at $1629\text{-}1642\text{ cm}^{-1}$ first intensified and then weakened with a shift from 1629 to

1642 cm^{-1} , which was attributed to the accumulation of quinoid intermediates (conjugated C=O overlapping aromatic C=C) followed by their deep oxidation and mineralization. These results confirm that prolonged mechanochemical treatment progressively destroyed the soil mineral structure while continuously generating surface oxygenated functional groups, thereby exposing reactive sites that facilitated PHE ring opening and mineralization.

Raman spectra (Fig. 3(e)) reflected the evolution of the carbon structure in soil samples at different ball milling times. The original sample showed only the G band of sp^2 carbon, whereas after ball milling the D band appeared, confirming the formation of amorphous carbon. The I_D/I_G values of samples treated for 0.5, 1, 2, and 3 h were 0.767, 0.811, 0.851, and 0.869, respectively, indicating that the disorder of the carbon structure and the amorphous carbon content gradually increased with prolonged MC treatment, reflecting the continuously enhanced carbonization of organic matter and pollutants under mechanical force. BET results (Fig. 3(f)) showed that all MC-treated soil samples exhibited type IV isotherms with H3-type hysteresis loops, and the N_2 adsorption capacity at low pressure was low, indicating that adsorption was dominated by mesopores. The desorption curve lay above the adsorption curve and did not coincide with it; the hysteresis loop exhibited H3 characteristics, revealing an open-boundary layered structure of the soil. The pore size distribution showed that with increasing ball milling time, the total nanopore volume of the soil decreased, resulting in a lower filling degree of nanopores and thereby weakening the adsorption of residual pollutants.

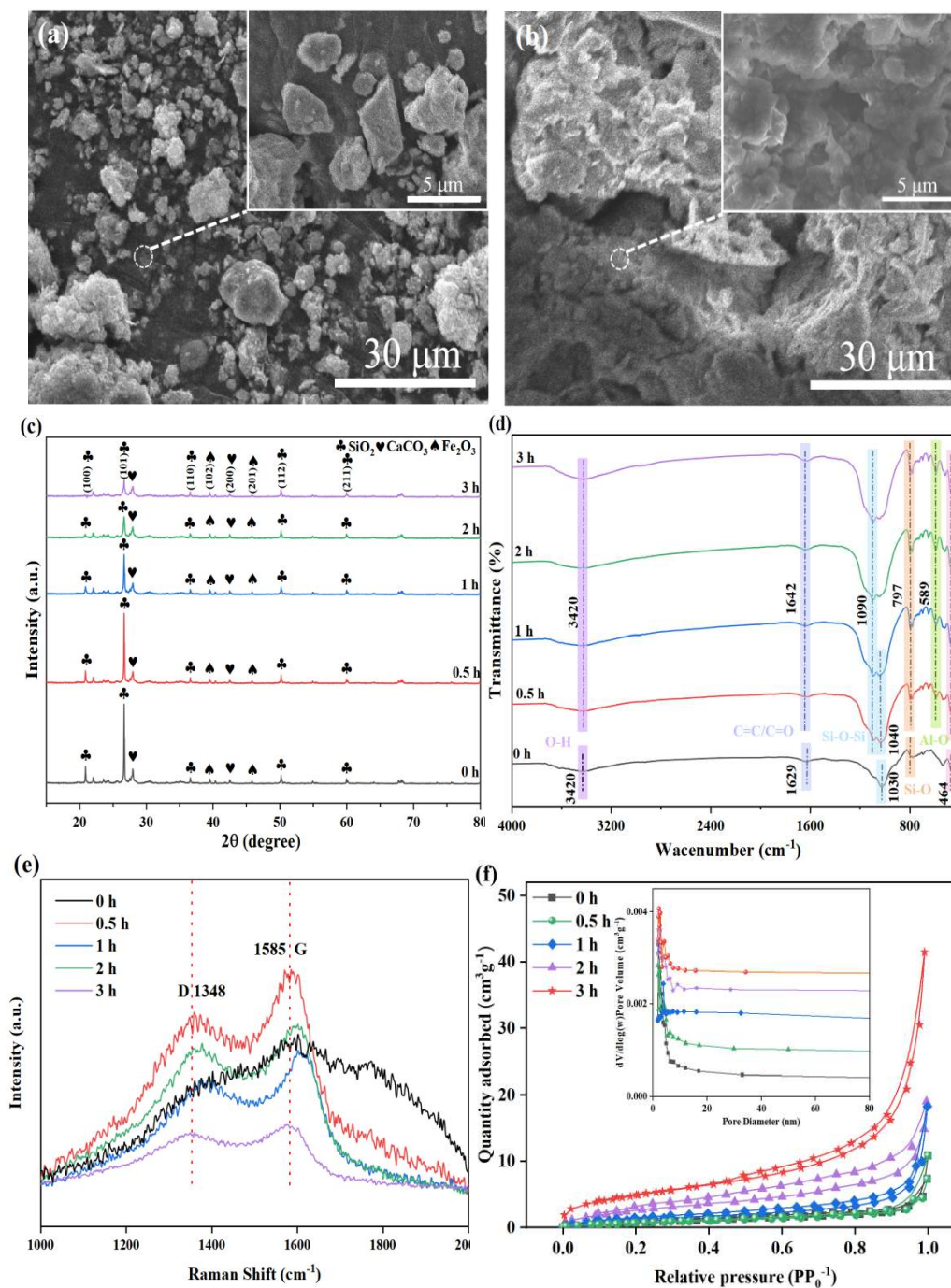


Fig. 3 (a) SEM image of the soil before ball milling; (b) SEM image of the soil after ball milling for 3 h; (c) XRD; (d) FTIR; (e) Raman; (f) BET. (Conditions: [PHE] = 0.2 mg·g⁻¹; MnO₂ = 0.5 g; rotation speed = 500 rpm; ball-to-material ratio = 25:1; grinding ball ratio = 4:6:1)

3.4 Degradation Pathway of PHE

Under the synergistic oxidation of MnO₂ and the mechanical force of ball milling, PHE first underwent epoxidation/hydration at the K-region (C9–C10), introducing

two hydroxyl groups to form cis-9,10-dihydroxy-9,10-dihydrophenanthrene (P1). P1 was further oxidized and dehydrated, converting the two hydroxyl groups into carbonyl groups to form phenanthrene-9,10-dione (P2) and thus realizing the transformation from an aromatic ring to a quinoid structure (Ji et al. 2021; Lee et al. 2020; Xie et al. 2022). Under continuous oxidation, P2 underwent cleavage and rearrangement of the C9–C10 bond to generate dibenzo[c,e]oxepine-5,7-dione (P3), achieving oxidative opening of the first benzene ring. P3 was then converted into [1,1'-biphenyl]-4,4'-dicarboxylic acid (P4) through lactone hydrolysis and aromatic ring cleavage. At this stage, the tricyclic skeleton of PHE had been degraded into a biphenyl-type dicarboxylic acid.

As a key node, P4 was transformed along three parallel pathways. (1) Cleavage of the biphenyl C–C bond occurred together with hydroxylation of the retained benzene ring, generating 3-hydroxyphthalic acid (P5); P5 was dehydroxylated to phthalic acid (P7), oxidatively decarboxylated to 2-hydroxybenzoic acid (P8), and finally dehydroxylated to benzoic acid (P9). (2) P4 underwent hydroxylation together with biphenyl bond cleavage to generate 2,5-dihydroxybenzoic acid (P6), which was directly dehydroxylated to salicylic acid (P8) and then to P9. (3) P4 directly underwent deep oxidative cleavage and decarboxylation to generate P9.

After hydroxylation of P9, the benzene ring was oxidatively opened to generate cis-(2Z,4Z)-hexa-2,4-dienedioic acid (P10), achieving complete cleavage of the single benzene ring. P10 was hydrogenated, during which the double bonds were saturated to generate adipic acid (P11). Further oxidative cleavage shortened the carbon chain to generate oxalic acid (P12), which was ultimately oxidized and mineralized to carbon dioxide and water, completing the thorough degradation of PHE.

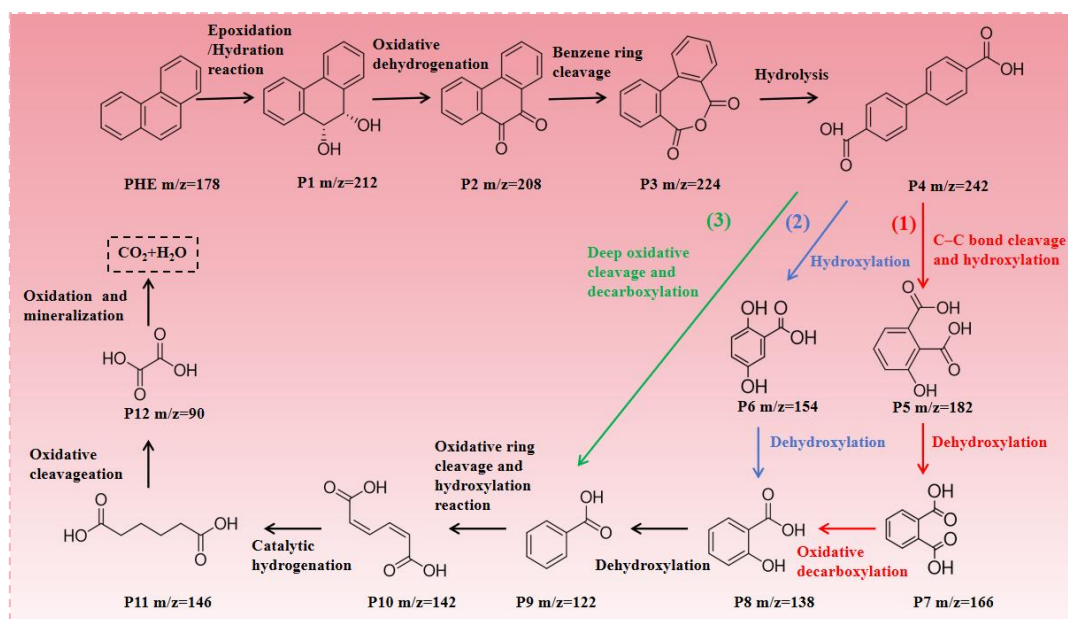
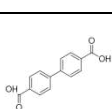
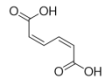
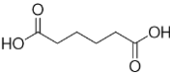
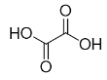


Fig. 4 Degradation pathway of PHE

Table 1 Information on the degradation intermediates of PHE

Number	Name	Chemical Formula	Structural Formula	m/z
PHE	phenanthrene	C ₁₄ H ₁₀		178
P1	cis-9,10-Dihydroxy-9,10-dihydrophenanthrene	C ₁₄ H ₁₂ O ₂		212
P2	phenanthrene-9,10-dione	C ₁₄ H ₈ O ₂		208
P3	dibenzo[c,e]oxepine-5,7-dione	C ₁₄ H ₈ O ₃		224
P4	[1,1'-biphenyl]-4,4'-dicarboxylic acid	C ₁₄ H ₁₀ O ₄		242
P5	3-hydroxyphthalic acid	C ₈ H ₆ O ₅		182
P6	2,5-dihydroxybenzoic acid	C ₇ H ₆ O ₄		154
P7	phthalic acid	C ₈ H ₆ O ₄		166
P8	2-hydroxybenzoic acid	C ₇ H ₆ O ₃		138
P9	benzoic acid	C ₇ H ₆ O ₂		122

P10	(2Z,4Z)-hexa-2,4-dienedioic acid	C ₆ H ₆ O ₄		142
P11	adipic acid	C ₆ H ₁₀ O ₄		146
P12	oxalic acid	C ₂ H ₂ O ₄		90

3.5 Toxicity Assessment

As shown in Fig. 5 (a), fish, daphnia, and green algae exhibited higher sensitivity to the acute toxicity of PHE and intermediates P1–P4. The acute toxicity values ranged from 1.15 to 4.15 mg·L⁻¹ for fish, 0.809 to 86.4 mg·L⁻¹ for daphnia, and 1.47 to 66.1 mg·L⁻¹ for green algae. Notably, compared with PHE (1.15, 0.809, and 1.47 mg·L⁻¹ for fish, daphnia, and green algae, respectively), the acute toxicity of intermediates P5–P9 was reduced, and as degradation progressed, the toxicity of P10–P12 continued to decrease to relatively low levels (Tang et al. 2025; Zhang et al. 2024b).

When chronic toxicity was considered, P5–P12 showed relatively lower toxicity than PHE, with P10–P12 exhibiting the lowest toxicity. These findings strongly indicate that MC can effectively reduce the ecotoxicity of PHE.(Murthy et al. 2024); therefore, to ensure ecological safety, complete mineralization of PHE must be guaranteed to avoid the accumulation of toxic intermediates.

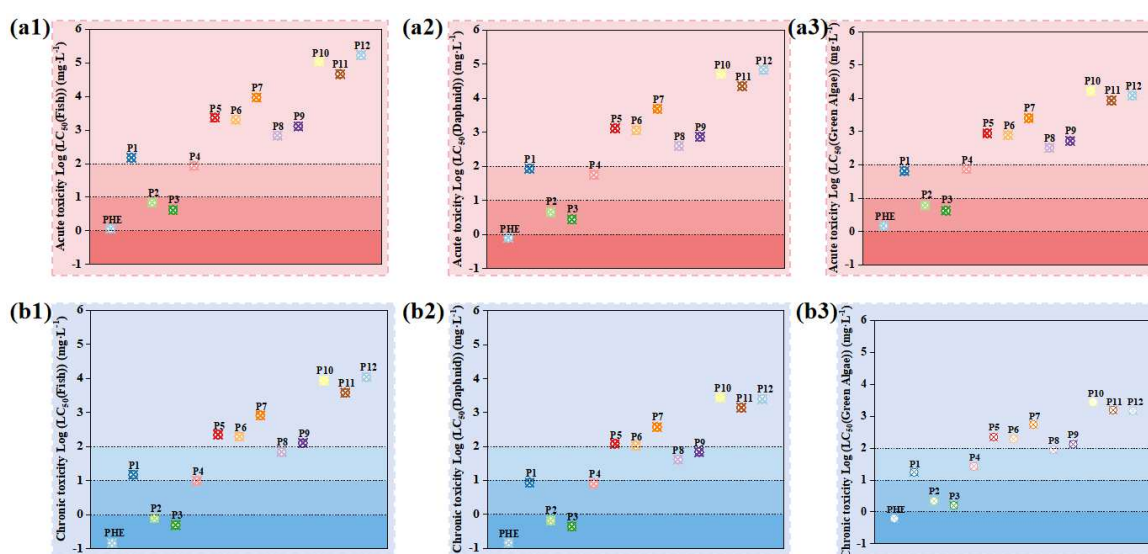


Fig. 5 (a) Acute toxicity of PHE and its degradation intermediates; (b) Chronic toxicity.

4 Conclusions

This study demonstrates that mechanochemical ball milling efficiently remediates PHE-contaminated soil. Among the milling aids tested, MnO_2 performed best, achieving a PHE degradation rate of 93.4% after 3 h—far exceeding the 43.1% without additives—because mechanically induced lattice distortion continuously generated $\cdot\text{OH}$ via the Mn(IV)/Mn(III) cycle. Under the optimized conditions of a 4:6:1 grinding ball ratio, a 25:1 ball-to-material ratio, and 500 rpm, the degradation rate approached 98%. Mechanistic analysis revealed that $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$, produced through one-electron reduction of O_2 by low-valent manganese and the piezoelectric effect, respectively, jointly drove PHE ring opening and mineralization along a pathway of aromatic hydrocarbon $\rightarrow$ quinone $\rightarrow$ biphenyl dicarboxylic acid $\rightarrow$ benzoic acid $\rightarrow$ ring-opened diene acid $\rightarrow$ short-chain fatty acid. Notably, the ecotoxicity of the degradation intermediates decreased significantly as the reaction progressed, ultimately reaching low or non-toxic levels.

References

- Adhami, S., Jamshidi-Zanjani, A., Darban, A.K. (2021). Phenanthrene removal from the contaminated soil using the electrokinetic-fenton method and persulfate as an oxidizing agent. *Chemosphere*, 266, 128988. <https://doi.org/10.1016/j.chemosphere.2020.128988>
- Chen, X., Li, Y., Fu, W., Tian, S., Yang, Y., Yang, K., et al (2023). Oriented generation of singlet oxygen in H_2O_2 activation for water decontamination: regulation of oxygen vacancies over $\alpha\text{-MnO}_2$ nanocatalysts. *Environmental Science: Nano*, 10, 1428-1440. <https://doi.org/10.1039/d3en00074e>
- Chu, L., Cang, L., Sun, Z., Wang, X., Fang, G., Gao, J. (2022). Reagent-free electrokinetic remediation coupled with anode oxidation for the treatment of phenanthrene polluted soil. *Journal of Hazardous Materials*, 433, 128724. <https://doi.org/10.1016/j.jhazmat.2022.128724>
- Deng, S., Liu, L., Cagnetta, G., Huang, J., Yu, G. (2021). Mechanochemically synthesized S-ZVIbm composites for the activation of persulfate in the pH-independent degradation of atrazine: effects of sulfur dose and ball-milling conditions. *Chemical Engineering Journal*, 423, 129789. <https://doi.org/10.1016/j.cej.2021.129789>
- Fan, G., Liu, X., Li, X., Lin, C., He, M., Ouyang, W. (2020). Mechanochemical treatment with CaO-activated PDS of HCB contaminated soils. *Chemosphere*, 257, 127207. <https://doi.org/10.1016/j.chemosphere.2020.127207>

- Guan, Y., Tang, X., Zhou, G., Ding, H., Huang, S., Chen, Q., et al (2026). Oxygen vacancy-engineered Mn_3O_4 for efficient activation of peroxydisulfate: dominant non-radical pathway in antibiotic degradation in aqueous systems. *Separation and Purification Technology*, 388, 136763. <https://doi.org/10.1016/j.seppur.2026.136763>
- Hu, X., Li, Q., Lin, X., Cheng, B., Cheng, Z., Yuan, X., et al (2025). Catalyzation of chlorine dioxide by manganese dioxide for efficient PAHs removal in industrial soil: new insight from relative reactive oxygen species generation. *Journal of Environmental Chemical Engineering*, 13, 117843. <https://doi.org/10.1016/j.jece.2025.117843>
- Ji, H., Liu, W., Sun, F., Huang, T., Chen, L., Liu, Y., et al (2021). Experimental evidences and theoretical calculations on phenanthrene degradation in a solar-light-driven photocatalysis system using silica aerogel supported TiO_2 nanoparticles: insights into reactive sites and energy evolution. *Chemical Engineering Journal*, 419, 129605. <https://doi.org/10.1016/j.cej.2021.129605>
- Ji, Y., Xu, J., Zhu, L. (2024). Redox potential model for guiding moderate oxidation of polycyclic aromatic hydrocarbons in soils. *Journal of Hazardous Materials*, 471, 134443. <https://doi.org/10.1016/j.jhazmat.2024.134443>
- Lee, H., Anwer, H., Park, J.W. (2020). Graphene quantum dots on stainless-steel nanotubes for enhanced photocatalytic degradation of phenanthrene under visible light. *Chemosphere*, 246, 125761. <https://doi.org/10.1016/j.chemosphere.2019.125761>
- Li, D., Zhao, Y., Wang, L., Wei, S., Huang, S. (2021a). Remediation of phenanthrene contaminated soil through persulfate oxidation coupled microbial fortification. *Journal of Environmental Chemical Engineering*, 9, 106098. <https://doi.org/10.1016/j.jece.2021.106098>
- Li, Q., Li, J., Jiang, L., Sun, Y., Luo, C., Zhang, G. (2021b). Diversity and structure of phenanthrene degrading bacterial communities associated with fungal bioremediation in petroleum contaminated soil. *Journal of Hazardous Materials*, 403, 123895. <https://doi.org/10.1016/j.jhazmat.2020.123895>
- Li, S., Tang, J., Yu, C., Liu, Q., Wang, L. (2022). Efficient degradation of anthracene in soil by carbon-coated nZVI activated persulfate. *Journal of Hazardous Materials*, 431, 128581. <https://doi.org/10.1016/j.jhazmat.2022.128581>
- Li, Z., Liang, J., Li, J., Ma, X., Lang, Y., Li, H., et al (2025). Thermal desorption coupled with persulfate oxidation for removing soil organic pollutants: key role of soil organic matter passivation. *Journal of Hazardous Materials*, 500, 140382. <https://doi.org/10.1016/j.jhazmat.2025.140382>
- Liang, J., Gao, S., Wu, Z., Rijnaarts, H.H., Grotenhuis, T. (2021). DNA-SIP identification of phenanthrene-degrading bacteria undergoing bioaugmentation and natural attenuation in petroleum-contaminated soil. *Chemosphere*, 266, 128984. <https://doi.org/10.1016/j.chemosphere.2020.128984>
- Liu, N., Zhou, X., Wu, L., Jin, T., Li, K., Wang, L. (2025). Remediation of various phenanthrene-contaminated soils using persulfate-*Pseudomonas aeruginosa* GZ7: Soil properties, radical formation, and microbial community. *Journal of Environmental Chemical Engineering*, 13, 115013. <https://doi.org/10.1016/j.jece.2024.115013>

- Lou, Z., Song, L., Liu, W., Chen, H., Yan, C., Yu, J., et al (2023). Sulfite as a green Co-milling agent for mechanochemical destruction of polychlorinated aromatics: working mechanism and structural dependence. *ACS ES&T Engineering*, 3, 944-954. <https://doi.org/10.1021/acsestengg.2c00403>
- Luo, Z., Min, Y., Qu, L., Song, Y., Hong, Y. (2021). Remediation of phenanthrene contaminated soil by ferrous oxalate and its phytotoxicity evaluation. *Chemosphere*, 265, 129070. <https://doi.org/10.1016/j.chemosphere.2020.129070>
- Meng, F.L., Zhang, X., Hu, Y., Sheng, G.P. (2024). New barrier role of iron plaque: producing interfacial hydroxyl radicals to degrade rhizosphere pollutants. *Environmental Science & Technology*, 58, 795-804. <https://doi.org/10.1021/acs.est.3c08132>
- Murthy, A.N., Rachitha, P., Sagar, N., et al (2024). Remediation of phenanthrene by highly efficient CdS–SnS photocatalyst and its cytotoxic assessments. *Chemosphere*, 355, 141790. <https://doi.org/10.1016/j.chemosphere.2024.141790>
- Pan, F., Ji, H., Du, P., Huang, T., Wang, C., Liu, W. (2021). Insights into catalytic activation of peroxymonosulfate for carbamazepine degradation by MnO₂ nanoparticles in-situ anchored titanate nanotubes: mechanism, ecotoxicity and DFT study. *Journal of Hazardous Materials*, 402, 123779. <https://doi.org/10.1016/j.jhazmat.2020.123779>
- Shen, X., Zhang, J., Xie, H., Sun, B., Liang, S., Wu, H., et al (2021). Electron shuttles enhance phenanthrene removal in constructed wetlands filled with manganese oxides-coated sands. *Chemical Engineering Journal*, 426, 131755. <https://doi.org/10.1016/j.cej.2021.131755>
- Shi, F.J., Feng, S.J., Niu, J.G., Zheng, Q.T., Zhang, X.L. (2025). A new in situ fracturing-enhanced oxidative remediation for various low-permeability phenanthrene-contaminated soils: oxidation effectiveness and kinetics of potassium permanganate. *Journal of Hazardous Materials*, 488, 137335. <https://doi.org/10.1016/j.jhazmat.2025.137335>
- Sleight, T.W., Khanna, V., Gilbertson, L.M., Ng, C.A. (2020). Network analysis for prioritizing biodegradation metabolites of polycyclic aromatic hydrocarbons. *Environmental Science & Technology*, 54, 10735-10744. <https://doi.org/10.1021/acs.est.0c02217>
- Song, L., Lin, L., Wei, W., Zhang, S., Wan, L., Lou, Z., et al (2023). Zero-valent iron-peroxydisulfate as synergistic co-milling agents for enhanced mechanochemical destruction of 2,4-dichlorophenol: coupling reduction with oxidation. *Journal of Environmental Management*, 345, 118571. <https://doi.org/10.1016/j.jenvman.2023.118571>
- Sun, Y., Niu, W.K., Hu, X.J., Ma, X.H., Sun, Y.J., Wen, Y. (2020). Oxidative degradation of polycyclic aromatic hydrocarbons in contaminated industrial soil using chlorine dioxide. *Chemical Engineering Journal*, 394, 124857. <https://doi.org/10.1016/j.cej.2020.124857>
- Sun, Z., Gu, Y., Zhang, X., Tong, Y., Chu, L., Cang, L., et al (2025). A novel electrokinetic flushing coupled with dual-anode system for enhanced PAHs removal from soil. *Journal of Environmental Management*, 396, 128130. <https://doi.org/10.1016/j.jenvman.2025.128130>
- Tang, Z., Xu, C., Shen, C., Meng, X., Xu, H., Li, F. (2025). Exploring the progressive change in transformation and toxicity of polycyclic dyes during aerobic biodegradation. *Journal of Hazardous Materials*, 488, 137465. <https://doi.org/10.1016/j.jhazmat.2025.137465>

- Tao, Y., Huang, H., Zhang, H. (2020). Remediation of Cu-phenanthrene co-contaminated soil by soil washing and subsequent photoelectrochemical process in presence of persulfate. *Journal of Hazardous Materials*, 400, 123111. <https://doi.org/10.1016/j.jhazmat.2020.123111>
- Wang, X., Cui, R., Shen, Y. (2025a). Mechanochemical remediation of POPs-contaminated soil using nano zero-valent iron (nZVI)-CaO-SiO₂. *Journal of Environmental Chemical Engineering*, 13, 119859. <https://doi.org/10.1016/j.jece.2025.119859>
- Wang, Y., Liu, M., Hu, C., Xin, Y., Ma, D., Gao, M., et al (2022). Enhanced MnO₂/peroxymonosulfate activation for phthalic acid esters degradation: regulation of oxygen vacancy. *Chemical Engineering Journal*, 433, 134048. <https://doi.org/10.1016/j.cej.2021.134048>
- Wang, Y., Ning, X., Liang, J., Wang, A., Qu, J. (2025b). Enhancing microbial superoxide generation and conversion to hydroxyl radicals for enhanced bioremediation using iron-binding ligands. *Journal of Environmental Sciences*, 147, 597-606. <https://doi.org/10.1016/j.jes.2023.11.023>
- Wang, Y., Tian, H., Zhang, C., Xu, J., Liu, X., Ma, F., et al (2024). Degradation and mechanism of PAHs by Fe-based activated persulfate: effect of temperature and noble metal. *Science of the Total Environment*, 931, 172768. <https://doi.org/10.1016/j.scitotenv.2024.172768>
- Wassenaar, P.N., Verbruggen, E.M. (2021). Persistence, bioaccumulation and toxicity-assessment of petroleum UVCBs: a case study on alkylated three-ring PAHs. *Chemosphere*, 276, 130113. <https://doi.org/10.1016/j.chemosphere.2021.130113>
- Wen, D., Zhu, Y., Wang, J., Ren, Y., Teng, W., Hu, J., et al (2026). Enhanced electroosmosis-induced delivery of persulfate for remediation of PAHs contaminated soil via time-modulated electric fields: a novel zoned processing concept. *Journal of Hazardous Materials*, 512, 142296. <https://doi.org/10.1016/j.jhazmat.2026.142296>
- Wu, D., Kan, H., Zhang, Y., Wang, T., Qu, G., Zhang, P., et al (2022). Pyrene contaminated soil remediation using microwave/magnetite activated persulfate oxidation. *Chemosphere*, 286, 131787. <https://doi.org/10.1016/j.chemosphere.2021.131787>
- Wu, M., Guo, X., Wu, J., Chen, K. (2020). Effect of compost amendment and bioaugmentation on PAH degradation and microbial community shifting in petroleum-contaminated soil. *Chemosphere*, 256, 126998. <https://doi.org/10.1016/j.chemosphere.2020.126998>
- Xia, M., Zhang, S., Xu, K., Zhang, C., Wang, X. (2025). Synergistic effects of adsorption and photocatalysis in MIL-88A(Fe) catalyst for remediation of phenanthrene-contaminated saline-alkaline soils. *Applied Catalysis A: General*, 689, 120010. <https://doi.org/10.1016/j.apcata.2024.120010>
- Xie, Z.H., He, C.S., Zhou, H.Y., Li, L.L., Liu, Y., Du, Y., et al (2022). Effects of molecular structure on organic contaminants' degradation Efficiency and dominant ROS in the advanced oxidation process with multiple ROS. *Environmental Science & Technology*, 56, 8784-8795. <https://doi.org/10.1021/acs.est.2c00464>
- Xu, H., Liu, X., Zhang, Z., Zhao, X., Lin, C., He, M., et al (2023). Peroxymonosulfate assisted

- mechanochemical remediation of high concentration DDTs contaminated soil. *Chemosphere*, 339, 139651. <https://doi.org/10.1016/j.chemosphere.2023.139651>
- Yang, M., Wen, Y., An, S., Zhao, Y., Fang, Z., Qiu, R., et al (2026). Zerovalent iron-loaded Biochar coupled with ball milling for perfluorooctanesulfonic acid remediation: synergistic capture and mechanochemical degradation. *Environmental Science & Technology*, 60, 17026-17036. <https://doi.org/10.1021/acs.est.6c03640>
- Yao, Z., He, X., Wang, Q., Wang, C., Shi, Q., Zhang, Q. (2023). Mechanochemical remediation of the chlorinated compounds contaminated soil depending on the minerals inside-the most reasonable approach. *Chemosphere*, 313, 137449. <https://doi.org/10.1016/j.chemosphere.2022.137449>
- Yi, Y., Kou, F., Tsang, P.E., Fang, Z. (2021). Highly efficient remediation of decabromodiphenyl ether-contaminated soil using mechanochemistry in the presence of additive and its mechanism. *Journal of Environmental Management*, 299, 113595. <https://doi.org/10.1016/j.jenvman.2021.113595>
- Yuan, W., Xie, J., Wang, X., Huang, Q., Huang, K. (2023). Mechanochemical remediation of soil contaminated with heavy metals and persistent organic pollutants by ball milling with nZVI-CaO-Ca₃(PO₄)₂ additives. *Chemical Engineering Journal*, 466, 143109. <https://doi.org/10.1016/j.ccej.2023.143109>
- Yue, X., Shan, Y., Jiao, W., Shen, K., Zhang, Y. (2023a). Role of direct current on thermal activated peroxydisulfate to degrade phenanthrene in soil: conversion of sulfate radical and hydroxyl radical to singlet oxygen, accelerated degradation rate and reduced efficiency. *Journal of Hazardous Materials*, 452, 131187. <https://doi.org/10.1016/j.jhazmat.2023.131187>
- Yue, X., Zhang, Y., Shan, Y., Shen, K., Jiao, W. (2023b). Lab-scale transport and activation of peroxydisulfate for phenanthrene degradation in soil: a comprehensive assessment of the remediation process, soil environment and microbial diversity. *Science of the Total Environment*, 901, 165771. <https://doi.org/10.1016/j.scitotenv.2023.165771>
- Zhang, B., Guo, Y., Huo, J., Xie, H., Xu, C., Liang, S. (2020). Combining chemical oxidation and bioremediation for petroleum polluted soil remediation by BC-nZVI activated persulfate. *Chemical Engineering Journal*, 382, 123055. <https://doi.org/10.1016/j.ccej.2019.123055>
- Zhang, C., Kong, C., Tratnyek, P.G., Qin, C. (2022). Generation of reactive oxygen species and degradation of pollutants in the Fe²⁺/O₂/tripolyphosphate system: regulated by the concentration ratio of Fe²⁺ and tripolyphosphate. *Environmental Science & Technology*, 56, 4367-4376. <https://doi.org/10.1021/acs.est.1c07467>
- Zhang, C., Tian, H., Wang, Z., Zhu, L., Liu, X., Wang, Y., et al (2023a). Degradation of PAHs in soil by activated persulfate system with activated carbon supported iron-based bimetal. *Science of the Total Environment*, 866, 161323. <https://doi.org/10.1016/j.scitotenv.2022.161323>
- Zhang, J., Han, K., Jiao, W., Su, P., Wang, D., Zhu, J., et al (2024a). Green mechanochemical activation of solid persulfate to remove PAHs in soil: performance and mechanism. *Journal of Hazardous Materials*, 472, 134489. <https://doi.org/10.1016/j.jhazmat.2024.134489>

- Zhang, J., Hu, X., Jiang, J., Wang, B., Zhang, Y. (2023b). Reinforced PAHs degradation in industrial site soil by Fe(III)/NaClO catalytic oxidation system: insights from promoting hydroxyl radicals generation. *Chemical Engineering Journal*, 474, 145785. <https://doi.org/10.1016/j.cej.2023.145785>
- Zhang, L., Wang, T., Zhang, M., Wang, L., Kang, G., Wu, S., et al (2024b). Ultrasonically activated persulfate process for the degradation of phenanthrene in soil-washing effluent: experimental, DFT calculation and toxicity evaluation. *Journal of Environmental Chemical Engineering*, 12, 113035. <https://doi.org/10.1016/j.jece.2024.113035>
- Zhang, Q., Meng, J., Su, G., Liu, Z., Shi, B., Wang, T. (2021a). Source apportionment and risk assessment for polycyclic aromatic hydrocarbons in soils at a typical coking plant. *Ecotoxicology and Environmental Safety*, 222, 112509. <https://doi.org/10.1016/j.ecoenv.2021.112509>
- Zhang, S., Li, H., He, R., Deng, W., Ma, S., Zhang, X., et al (2023c). Spatial distribution, source identification, and human health risk assessment of PAHs and their derivatives in soils nearby the coke plants. *Science of the Total Environment*, 861, 160588. <https://doi.org/10.1016/j.scitotenv.2022.160588>
- Zhang, S., Zhang, S., Liu, Z., Yan, K. (2024c). Mechanochemical remediation of 3,4,3',4'-tetrachlorobiphenyl (PCB77) contaminated soil by ball milling and a novel technology combining ball milling with dielectric barrier discharge. *Chemical Engineering Journal*, 497, 154398. <https://doi.org/10.1016/j.cej.2024.154398>
- Zhang, S., Zhao, J., Zhu, L. (2024d). New insights into thermal desorption remediation of pyrene-contaminated soil based on an optimized numerical model. *Journal of Hazardous Materials*, 461, 132687. <https://doi.org/10.1016/j.jhazmat.2023.132687>
- Zhang, X., Liu, X., Zhao, J., Sun, W., Li, X., Li, J., et al (2021b). NaOH-activated persulfate-assisted mechanochemical mechanism and removal of lindane from contaminated soil. *Journal of Environmental Chemical Engineering*, 9, 105391. <https://doi.org/10.1016/j.jece.2021.105391>
- Zhang, Z., Mao, L., Liu, X., Zhao, X., Lin, C., He, M., et al (2024e). Mechanochemical degradation performance of lindane in different types of soils: the effects of soil properties and elemental components. *Science of the Total Environment*, 918, 170422. <https://doi.org/10.1016/j.scitotenv.2024.170422>
- Zhang, Z., Zhou, Z., Liu, X., Zhang, H., Xu, H., Lin, C., et al (2023d). Mechanochemical remediation of lindane-contaminated soils assisted by CaO: performance, mechanism and overall assessment. *Journal of Hazardous Materials*, 458, 131985. <https://doi.org/10.1016/j.jhazmat.2023.131985>
- Zhao, X., Xu, H., Zhang, Z., Zhao, Y., Liu, X., Lin, C., et al (2026). Pilot-scale treatment of highly concentrated chlorinated organic contaminated soil via a horizontal planetary ball mill system. *Journal of Environmental Chemical Engineering*, 14, 122313. <https://doi.org/10.1016/j.jece.2026.122313>

Declarations

Ethics approval and consent to participate

This study did not involve human participants, human data, or animal subjects. All work was conducted on materials, processes, and computational models. Therefore, ethical approval and consent to participate were not required for this research.

Consent for publication

All authors consent to the submission and approve the final version.

Availability of data and material

All data generated or analyzed during this study are included in this published article. The authors confirm that the manuscript is original, has not been published before, and is not currently under review elsewhere.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This work was supported by Scientific Research Fund of Liaoning Provincial Education Department (Project ID: LJ212510148008 and LJ212410148003); Jointly Planned Project of the Liaoning Provincial Department of Science and Technology (Project ID: 2025-MSLH-442); Liaoning Province Frontier Technology Research and Development Program (Project ID: 2026JH40/10100011).

Author contributions

Tao Zhang[#]: Conceptualization, Data curation, Writing- original draft.

Guizhou Gu[#]: Conceptualization, writing-review and editing, Funding acquisition.

Xin Wang: Data curation, Writing- original draft.

Xiaona Wei: Writing-review and editing, Funding acquisition.

Zheng Li^{*}: Review and editing, Project administration, Funding acquisition.

Changfei Gao^{*}: Supervision, Project administration, Funding acquisition.