

Mechanistic and Kinetic Insights into Time-Dependent Fenton Oxidation Pathways for Polycyclic Aromatic Hydrocarbon Degradation in Crude Oil-Contaminated Soils

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Despite the widespread application of Fenton oxidation for hydrocarbon remediation, the time-dependent kinetic transition between matrix-limited and radical-dominated degradation regimes in crude oil-contaminated soils remains insufficiently resolved. This study systematically investigated long-term (60-day) PAH degradation under controlled batch Fenton oxidation using Fe²⁺-activated H₂O₂ at concentrations of 5–40 ppm. The degradation process was evaluated relative to natural attenuation. GC–MS quantification was integrated with pseudo-first-order kinetic modeling to elucidate the degradation dynamics. Natural attenuation produced moderate PAH reduction (≈42% in crude oil matrix and 85.7% in contaminated soil), reflecting matrix-governed constraints on bioavailability and oxidative transformation. Fenton treatment significantly enhanced degradation in a concentration-dependent manner, achieving >99.4% removal at 40 ppm. Apparent rate constants remained comparable at 5–30 ppm (0.0290–0.0317 day⁻¹) but increased markedly at 40 ppm (0.0853 day⁻¹; R² = 0.970; p < 0.05), indicating a statistically significant kinetic regime shift. This transition suggests reduced scavenging dominance and improved hydroxyl radical availability rather than simple linear oxidant acceleration. Degradation behavior was consistent with established hydroxyl radical-mediated pathways involving aromatic hydroxylation and progressive ring destabilization. By quantitatively identifying an oxidant threshold beyond which radical control supersedes matrix limitation, this study advances predictive understanding of dose-dependent Fenton reactivity in heterogeneous soil systems

and provides mechanistically informed guidance for optimizing PAH remediation strategies.

Keywords: Fenton oxidation; Polycyclic aromatic hydrocarbons (PAHs); Contaminated soil; Oxidation kinetics; Pseudo-first-order modeling; Soil remediation

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1.0 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most persistent organic contaminants in terrestrial environments (Edet *et al.*, 2021; Soleimani *et al.*, 2024). They are also considered highly hazardous due to their toxicity and potential carcinogenicity (Srivastava *et al.*, 2025; Sule *et al.*, 2023). Their occurrence is particularly pronounced in soils impacted by crude oil exploration, transportation, and spillage (Chakravarty *et al.*, 2022; Edet *et al.*, 2021; Olawoyin, *et al.*, 2012; Adesina, *et al.*, 2023). These compounds comprise fused aromatic rings with varying molecular weights. Higher molecular weight PAHs (≥4 rings) are especially recalcitrant due to their strong hydrophobicity, low aqueous solubility, and pronounced sorption to soil organic matter (Owabor *et al.*, 2012; Ukalska-Jaruga *et al.*, 2019) low aqueous solubility (Valdivieso Quintero and Zafra, 2016), and pronounced sorption to soil organic matter (Tao

et al., 2009; Makkar and Rockne, 2003). As a result, PAHs exhibit prolonged residence times in soil matrices and pose significant ecological and human health risks, including mutagenic and carcinogenic effects (Usman *et al.*, 2016; Srivastava *et al.*, 2025; Sule *et al.*, 2023). In crude oil-contaminated soils, aging processes reduce PAH bioavailability, rendering natural attenuation and conventional remediation strategies insufficient for effective risk reduction (Dandie *et al.*, 2010; Henry, 2004; García-Sánchez *et al.*, 2018).

Advanced oxidation processes (AOPs), particularly Fenton oxidation, have attracted considerable attention as promising remediation techniques capable of overcoming these limitations (Mukherjee *et al.*, 2023; Pushpalatha & Krishna 2017; Ameta *et al.* 2018). The classical Fenton reaction involves the catalytic decomposition of hydrogen peroxide by ferrous iron (Fe^{2+}), generating highly reactive hydroxyl radicals ($\bullet\text{OH}$) that non-selectively attack aromatic systems. However, these studies are often conducted under simplified laboratory conditions that may not adequately capture the physicochemical complexity of real contaminated soils (Goi & Trapido, 2004; Smara *et al.*, 2024). However, the practical application of Fenton processes to real soils remains constrained by factors such as heterogeneous contaminant distribution (Usman *et al.*, 2016; Checa-Fernandez *et al.*, 2021), radical scavenging by natural organic matter (Lemaire, 2011; Usman *et al.*, 2016), limited contaminant accessibility (Zhao *et al.*, 2019; Satilmis & Schrader, 2022), and incomplete mineralization of complex PAH structures (Usman *et al.*, 2012; Lemaire, 2011). From a mechanistic standpoint, hydroxyl radical attack initiates PAH transformation through aromatic ring hydroxylation. This is followed by oxidative ring opening and subsequent formation of oxygenated intermediates. Despite this general understanding, many existing studies focus

primarily on short reaction times, slurry-based systems, or overall removal efficiencies, with limited emphasis on time-dependent reaction pathways and kinetic transitions in soil environments. Consequently, the relationship between oxidant dosage, degradation kinetics, and mechanistic progression from partial oxidation to complete aromatic ring destruction remains insufficiently resolved, particularly for crude oil-contaminated soils that better represent field conditions. Therefore, a critical knowledge gap exists in understanding how oxidant concentration governs the transition between matrix-limited and radical-dominated degradation regimes over extended treatment periods in realistic soil systems.

Kinetic modeling plays a critical role in bridging this gap by providing quantitative insight into reaction rates, rate-controlling steps, and oxidant efficiency. Such integration is essential for distinguishing whether observed increases in degradation efficiency arise from true mechanistic shifts or merely from enhanced oxidant availability. Previous investigations commonly describe PAH degradation under Fenton conditions using pseudo-first-order kinetic models, reporting rate constants that vary with oxidant concentration, iron availability, and soil characteristics (Valderrama *et al.*, 2009; Smara *et al.*, 2024). However, in many cases, kinetic analysis is treated as a secondary descriptive tool rather than being explicitly linked to underlying reaction mechanisms. As a result, it remains unclear how changes in oxidant concentration influence not only degradation rates but also the dominant oxidative pathways governing PAH transformation and mineralization over extended treatment periods.

This study aims to investigate the time-dependent kinetic and mechanistic transitions governing PAH degradation under varying Fenton oxidant concentrations in crude oil-



contaminated soils. By examining time-resolved PAH degradation “under controlled batch conditions over an extended treatment period, this work establishes clear links between oxidant dosage, pseudo-first-order kinetic behavior, and hydroxyl radical-driven degradation pathways. The study advances current understanding by demonstrating how increasing oxidant availability shifts the degradation regime from partial oxidation and intermediate accumulation toward rapid aromatic ring cleavage and near-complete mineralization. These findings provide a mechanistically grounded basis for optimizing Fenton oxidation processes and support the development of more efficient, field-relevant remediation strategies for PAH-contaminated soils.

2.0 Materials and Methods

2.1 Study Design and Experimental Framework

This study was designed to elucidate the time-dependent degradation kinetics and mechanistic behavior of polycyclic aromatic hydrocarbons (PAHs) in crude oil-contaminated soil under Fenton oxidation conditions. A controlled factorial experimental design was employed to evaluate the influence of oxidant concentration and reaction time on hydrocarbon removal efficiency. Five Fenton reagent concentrations (5, 10, 20, 30, and 40 ppm) were investigated across five reaction intervals (1, 7, 14, 30, and 60 days), thereby enabling assessment of both the main and interaction effects of oxidant concentration and reaction time on degradation dynamics.. All treatments were performed in triplicate to ensure statistical reliability, and untreated contaminated soil served as the experimental control. Raw crude oil and unpolluted soil were analyzed as reference matrices for baseline hydrocarbon characterization.

2.2 Soil Sampling and Preparation

Surface soil samples were collected from reserved land within the National Root Crop

Research Institute (NRCRI), Umudike, Nigeria. Sampling was conducted at five independent locations at depths ranging from 5 ± 1 cm to 15 ± 1 cm to obtain representative samples. The samples were homogenized to produce a composite matrix weighing approximately 40 kg. Visible debris, stones, and plant materials were removed manually. The soil was air-dried under ambient laboratory conditions and sieved to obtain a uniform particle size distribution prior to contamination and treatment. .

2.3 Artificial Contamination Procedure

To simulate petroleum-polluted soil, 35 kg of the prepared composite soil was spiked with 700 mL of Bonny Light crude oil, corresponding to approximately 2% (w/w) contamination relative to soil mass. The mixture was mechanically stirred to achieve homogeneity and ensure uniform hydrocarbon distribution within the soil matrix. The contaminated soil was subsequently divided into 6 kg portions and stored in 7 L inert (polyethylene) containers before oxidation treatment. This controlled contamination protocol ensured reproducibility and minimized variability in initial hydrocarbon concentration.

2.4 Preparation of the Fenton System

All reagents used were of analytical grade. Iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) served as the ferrous ion source, while 30% hydrogen peroxide (H_2O_2) functioned as the oxidant. The Fenton system operates via catalytic decomposition of hydrogen peroxide, generating highly reactive hydroxyl radicals ($\bullet\text{OH}$) capable of non-selective oxidation of organic contaminants. The fundamental reaction mechanism involves the oxidation of Fe^{2+} to Fe^{3+} with concurrent production of hydroxyl radicals, followed by partial regeneration of Fe^{2+} through reaction with additional hydrogen peroxide.

A 100 ppm Fe^{2+} stock solution was prepared by dissolving 0.2205 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled



water. Hydrogen peroxide (30%) was added separately to initiate the Fenton reaction. Working concentrations (5, 10, 20, 30, and 40 ppm Fe^{2+}) were prepared by appropriate dilution of the iron stock solution prior to treatment.

2.5 Oxidative Treatment of Contaminated Soil

For each experimental condition, 1 kg of contaminated soil was transferred into glass reactors and treated with the designated Fenton reagent concentration. The oxidant was uniformly applied to the soil surface and thoroughly mixed to promote intimate contact between reactive radicals and hydrocarbon substrates. Treated samples were maintained under ambient laboratory conditions throughout the designated reaction periods of 1, 7, 14, 30, and 60 days. Moisture levels were periodically monitored and maintained to minimize variability in mass transfer and diffusion-controlled processes. At the end of each exposure interval, samples were collected for hydrocarbon extraction and analysis. This systematic approach allowed assessment of temporal degradation patterns and concentration-dependent oxidative efficiency.

2.6 Extraction and Quantitative Determination of Hydrocarbons

Hydrocarbon extraction was conducted in accordance with United States Environmental Protection Agency (USEPA) Method 3540C for non-volatile and semi-volatile organic compounds. Approximately 10 g of treated soil was mixed with an equal mass of anhydrous sodium sulfate to eliminate residual moisture and transferred into an extraction thimble. Soxhlet extraction was performed using 150 mL of acetone/dichloromethane (1:1 v/v) for two hours at a rate of 4–6 cycles per hour. Extracts were cooled and passed through a drying column containing anhydrous sodium sulfate to remove residual water. The eluate was gently concentrated to approximately 1 mL

without allowing complete dryness to prevent analyte loss.

Quantitative determination of PAHs was performed using gas chromatography equipped with a flame ionization detector (GC-FID; Agilent 6890N series), following USEPA Method 8015. Calibration curves were constructed using certified hydrocarbon standards, and analytical quality control included procedural blanks, duplicate samples, and recovery assessments. Detection and quantification limits were determined based on signal-to-noise criteria. Samples were stored at temperatures below 4°C prior to analysis to preserve chemical integrity.

Removal efficiency was calculated using:

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the PAH concentration at Day 1 and C_t is the concentration at time t .

2.7 Kinetic Modeling and Degradation Analysis

The degradation kinetics of PAHs were evaluated using a pseudo-first-order model:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (2)$$

where C is the PAH concentration at time t , C_0 is the initial concentration, and k is the apparent pseudo-first-order rate constant (day^{-1}).

Linear regression analysis was performed using statistical software (OriginPro), and rate constants were determined from the slope of $\ln(C/C_0)$ versus time plots. Coefficients of determination (R^2) were used to assess model fit. For systems exhibiting first-order behavior, half-life values were calculated to quantify degradation efficiency and enable comparative evaluation across treatment conditions using equation 3

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

2.9 Statistical Analysis

All experiments were conducted in triplicate, and results are reported as mean \pm standard deviation. Two-way analysis of variance (ANOVA) was applied to evaluate the



individual and interactive effects of oxidant concentration and reaction time on hydrocarbon removal efficiency. Statistical analyses were conducted and significance was defined at $p < 0.05$.

3.0 Results and Discussion

3.1 Natural Attenuation of PAHs in Crude Oil and Polluted Soil

The natural attenuation profiles of PAH contamination in crude oil and soil over 60 days, as presented in Table 1 and Fig. 1, reveal a markedly slower degradation trajectory for crude oil compared with polluted soil. In the crude oil sample, PAH concentrations decreased gradually from 7420 mg/kg on day 1 to 4291 mg/kg by day 60 representing approximately a 42% reduction. This indicates a slow degradation process with substantial persistence of aromatic hydrocarbons. It also reflects the inherent recalcitrance of PAHs in oil matrices, where limited oxygen availability, reduced microbial accessibility, and strong hydrophobic interactions inhibit rapid degradation. In contrast, polluted soil exhibited a much steeper decline in PAH concentration, decreasing from 265 mg/kg on day 1 to 38 mg/kg at day 60, corresponding to an 85.7% reduction over the same period. The sharper decay curve observed in Fig. 1 for polluted soil highlights the enhanced role of soil-mediated processes, including microbial activity, moisture availability, and surface-mediated oxidation reactions. Although the two systems differ in initial PAH concentration and physicochemical characteristics, the observed trends suggest that matrix effects, including bioavailability and sorption, play an important role in controlling PAH degradation. This pattern aligns with the well-documented recalcitrance of PAHs in hydrophobic matrices,

where limited bioavailability and strong sorption constrain natural degradation processes. Similar trends have been reported in field-scale soil studies, where prolonged persistence of high-molecular-weight PAHs was linked to strong soil binding and low microbial accessibility (Smara *et al.*, 2024). The exponential decay shape of the concentration–time curves in Fig. 1 supports pseudo-first-order modeling, consistent with natural attenuation patterns described in hydrocarbon-contaminated environments (goi and trapido, 2004). However, the relatively slow degradation rate highlights the limitation of natural attenuation as a standalone remediation strategy for heavily contaminated environments, particularly where rapid risk reduction is required. Table 1 shows the *natural attenuation* of PAHs over 60 days.

The influence of Fenton oxidation on PAH degradation is summarized in Table 2 and visualized in Fig. 2. Application of Fenton's reagent resulted in a dramatic acceleration of PAH removal across all oxidant concentrations investigated. Compared to the untreated control soil, which retained 38.01 ± 2.00 mg/kg PAHs after 60 days, all Fenton-treated samples exhibited significantly lower residual concentrations. At lower oxidant concentrations (5–20 ppm), PAH degradation was substantial but gradual, with final concentrations ranging from 4.44 to 3.87 mg/kg after 60 days. Increasing the oxidant concentration to 30 ppm further enhanced degradation efficiency, yielding a final PAH concentration of 2.90 mg/kg. Notably, treatment with 40 ppm oxidant resulted in near-complete removal, reducing PAH concentration to 0.10 ± 0.02 mg kg⁻¹ by day 60.

Table 1: Levels of natural attenuation of PAHs over 60 days

Sample	Initial Conc.	Day 7	Day 14	Day 30	Day 60
Crude Oil (mg/kg)	7420.67 ± 29.28	7125.68 ± 26.41	6671.67 ± 24.58	5482 ± 22.00	4291 ± 29.05
Polluted Soil	265 ± 6.00	77.00 ± 3.00	64.67 ± 2.52	47.33 ± 1.53	38.00 ± 2.00
Raw Soil	< 0.001	-	-	-	-



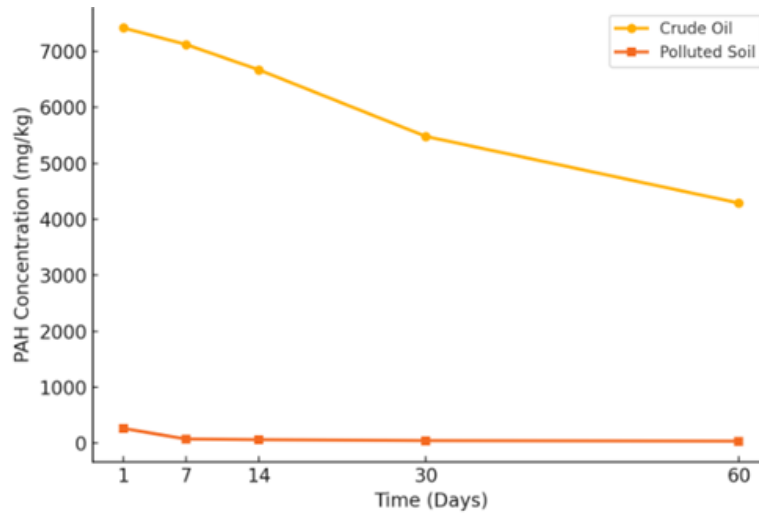


Fig. 1: Natural degradation of PAHs

3.2 Effect of Fenton’s Reagent on PAH Degradation

These trends are clearly reflected in Fig. 2, where the degradation curves become progressively steeper with increasing oxidant dosage. The concentration-dependent enhancement observed corroborates the central role of hydroxyl radicals in oxidizing persistent organic contaminants. Higher oxidant concentrations promote greater production of [•]OH radicals, which rapidly attack the aromatic structures of PAHs, leading to accelerated breakdown. Importantly, the diminishing separation between curves at later stages suggests that, at sufficiently high oxidant levels, the reaction shifts toward more extensive oxidation and reduced intermediate accumulation. This concentration-dependent enhancement mirrors observations by Smara and colleagues, who reported Fenton processes achieving 84.7% to 99.9% PAH removal in contaminated soils, with oxidant dosing being a key determinant of reaction rate and extent (Smara *et al.*, 2024). The trends seen in Fig. 2 also reflect the known dependency of Fenton oxidation efficacy on adequate hydroxyl radical generation, as excessive radical production increases aromatic ring attack and subsequent mineralization (Usman *et al.*, 2016).

The near-complete degradation reached at 40 ppm across 60 days in this study is particularly notable. The 40 ppm treatment achieved near-complete degradation (>99.4%) by day 60 (Table 3), demonstrating the efficacy of Fenton oxidation as a powerful advanced oxidation process for PAH remediation. While some earlier works have achieved high removal efficiencies in shorter timeframes, such rapid degradation often occurs under controlled slurry conditions or with optimized molar ratios of H₂O₂/Fe²⁺.

Table 2 presents degradation under varying Fenton's reagent concentrations (oxidant)

Oxidant (ppm)	Day 1	Day 7	Day 14	Day 30	Day 60
0 ppm	265.00 ± 6.00	77.00 ± 3.00	63.67 ± 2.52	47.33 ± 1.53	38.00 ± 2.00
5 ppm	37.40 ± 0.66	18.63 ± 0.55	10.17 ± 0.35	7.16 ± 0.13	4.44 ± 0.14
10 ppm	32.63 ± 0.75	16.87 ± 0.45	8.87 ± 0.25	6.21 ± 0.13	4.03 ± 0.14
20 ppm	26.40 ± 0.66	16.37 ± 0.45	7.10 ± 0.30	6.04 ± 0.13	3.87 ± 0.14
30 ppm	24.77 ± 0.65	11.67 ± 0.35	6.33 ± 0.25	5.48 ± 0.14	2.90 ± 0.15
40 ppm	19.53 ± 0.55	10.30 ± 0.40	4.60 ± 0.20	2.90 ± 0.11	0.10 ± 0.02

**Values represent mean ± standard deviation (n = 3).



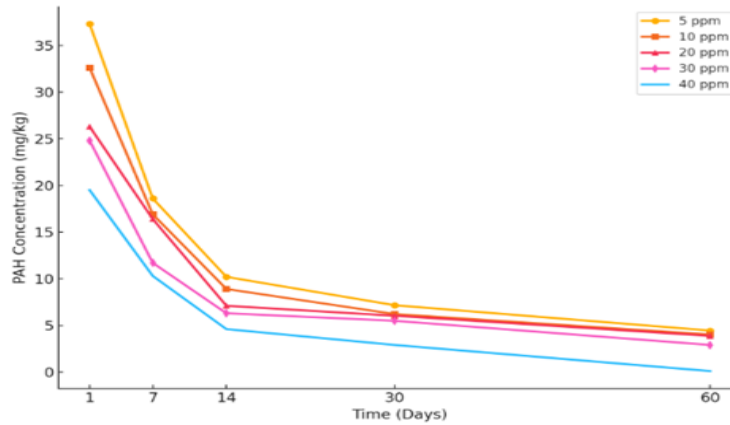


Fig. 2: PAH degradation under Fenton oxidation

Other reports indicate up to ~80% PAH removal within hours to days when using enhanced Fenton or modified systems (e.g., citric-Fenton), but these conditions often require precise pH control or chelating agents to maintain iron solubility (Zhao *et al.*, 2019). These results align well with these patterns and extend them by demonstrating long-term oxidative removal in a soil context where natural buffering, soil heterogeneity, and contaminant accessibility present real application challenges.

To quantitatively evaluate the influence of operational variables, a two-way analysis of variance (ANOVA) was performed considering oxidant concentration and reaction time as independent factors. The two-way ANOVA in Table 4 revealed that both Fenton reagent concentration and reaction time significantly influenced PAH degradation ($p < 0.0001$). Reaction time exhibited the strongest statistical effect on PAH removal ($F = 10447.22$),

indicating that degradation progressed strongly with increasing exposure duration. The interaction between oxidant concentration and reaction time was also statistically significant ($F = 118.01, p < 0.0001$), suggesting that the effect of oxidant dosage on PAH removal depends on the duration of treatment. This interaction indicates that higher oxidant concentrations become increasingly effective as the reaction proceeds.

3.3 Kinetic Model Validation and Rate Enhancement

The kinetic interpretation of the Fenton oxidation process is supported by the pseudo-first-order kinetic parameters presented in Table 5 and the semi-logarithmic plots shown in Fig. 3. Linear relationships between $\ln(C/C_0)$ and time were observed for all oxidant concentrations, confirming that PAH degradation under Fenton treatment follows pseudo-first-order kinetics. The calculated rate constants reveal a clear dependence on oxidant concentration.

Table 3: PAH Removal Efficiency (%) During Fenton Oxidation

Oxidant (ppm)	Day 7 (%)	Day 14 (%)	Day 30 (%)	Day 60 (%)
0	70.94	75.97	82.26	85.66
5	50.19	72.73	80.86	88.10
10	48.27	72.73	80.97	87.67
20	37.64	73.00	77.08	85.29
30	52.82	74.60	77.86	88.31
40	47.31	76.43	85.13	99.49



Table 4: Two-Way ANOVA for Effects of Fenton Concentration and Reaction Time on PAH Degradation

Source of Variation	Sum of Squares	df	F-value	p-value
Fenton concentration	583.87	4	990.70	< 0.0001
Reaction time	6157.06	4	10447.22	< 0.0001
Concentration × Time	278.20	16	118.01	< 0.0001
Residual (Error)	7.37	50	—	—
Total	7026.50	74	—	—

Treatments between 5 and 30 ppm exhibited comparable rate constants (0.0290–0.0317 day⁻¹), suggesting that, within this range, degradation may be partially limited by soil matrix effects, radical scavenging by natural organic matter, or diffusion constraints. The moderate R² values suggest deviations from ideal first-order behavior, likely due to heterogeneity, diffusion limitations, and competing reactions within the soil matrix.

Jorfi *et al.* earlier demonstrated similar pseudo-first-order behavior, noting that higher reagent concentrations accelerated contaminant degradation (Jorfi *et al.*, 2013). While your system exhibits longer degradation times compared with controlled slurry systems, the underlying kinetic consistency reinforces the broader applicability of Fenton oxidation for real-world contaminated soils.

Table 5. Pseudo-first-order kinetic parameters for PAH degradation under Fenton oxidation

Oxidant concentration	Rate constant, k (day ⁻¹)	R ²	Half-life (days)
5 ppm	0.0317	0.816	17.8
10 ppm	0.0314	0.807	18.2
20 ppm	0.0290	0.776	20.4
30 ppm	0.0309	0.805	16.5
40 ppm	0.0853	0.970	7.79

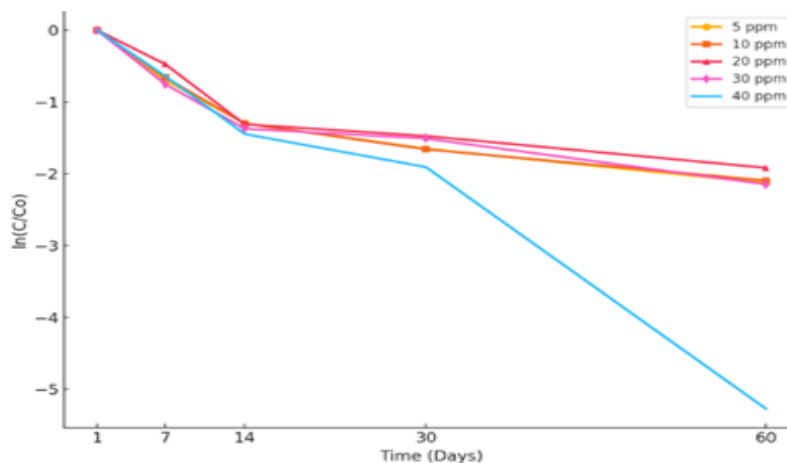


Fig. 3: Pseudo-first order kinetics for all Fenton oxidant concentrations

In contrast, the 40ppm treatment displayed a substantially higher rate constant of 0.0853

day⁻¹ and an excellent coefficient of determination (R² = 0.970). Higher R² values at



40 ppm reflect more ideal pseudo-first-order behavior, consistent with previous kinetic observations in Fenton systems. For example, earlier studies have reported pseudo-first-order kinetics in both slurry and soil systems, with the rate constant values dependent on oxidant dosage and soil characteristics (Zhao, *et al.*, 2019). This result indicates that, at elevated oxidant loading, hydroxyl radical generation

may be sufficient to dominate competing reactions, leading to rapid and kinetically predictable PAH degradation. The tight linearity observed in Fig. 3 for the 40 ppm system strongly supports a regime likely dominated by hydroxyl radical reactions. Variability in rate constants may also reflect heterogeneity in contaminant distribution and soil microenvironments

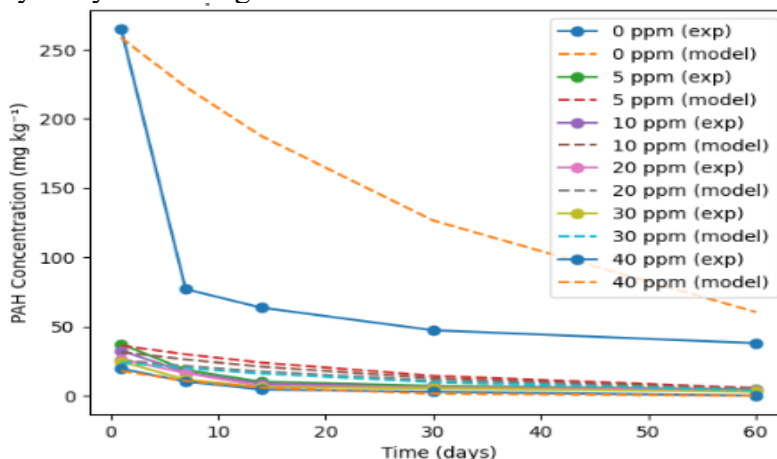


Fig. 4: Experimental vs pseudo-first-order kinetic model fit

The reliability of the proposed kinetic model was assessed by comparing, experimental concentration data with model-predicted values derived from the pseudo-first-order equation as presented in Fig. 4. The curves demonstrate good agreement between experimental observations and model predictions. The close overlap between experimental and predicted curves suggests that the pseudo-first-order model adequately captures the essential kinetics of the oxidation process. Minor deviations observed at later stages of the reaction may reflect diffusion limitations, radical scavenging by soil organic matter, or secondary transformation reactions of intermediate products. These findings show that the degradation of PAHs during Fenton oxidation in crude oil-contaminated soils can be effectively described using a first-order kinetic framework.

4.0 Conclusion

This study investigated the time-dependent degradation kinetics and mechanistic pathways

of polycyclic aromatic hydrocarbons (PAHs) in crude oil-contaminated soils under Fenton oxidation conditions. Natural attenuation proceeded slowly and was strongly influenced by matrix effects, confirming the limited efficiency of passive remediation strategies for persistent PAHs. In contrast, Fenton oxidation significantly enhanced PAH removal, achieving near-complete degradation at higher oxidant concentrations through hydroxyl radical-driven pathways. Kinetic modeling demonstrated that PAH degradation followed pseudo-first-order kinetics, with rate constants increasing markedly at elevated oxidant dosages and exhibiting strong model fit. The concentration-dependent kinetic enhancement highlights hydroxyl radical availability as a key rate-controlling factor governing aromatic ring transformation and extensive oxidation. Mechanistic analysis further suggests that sequential hydroxylation and oxidative ring opening underpin the observed degradation trends. Overall, the findings establish Fenton



oxidation as a rapid, kinetically predictable, and mechanistically robust approach for the remediation of PAH-contaminated soils under environmentally relevant conditions. Future studies should focus on optimizing operational parameters and validating performance under field-scale conditions.

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Declarations

Ethics and Consent to Participate
Not applicable.

Consent to Publish

Not applicable

Availability of data and materials

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Authors' Contributions

Kerian K. Dingba conducted the experimental work, data collection, kinetic modeling, statistical analysis, and initial manuscript drafting. Babatunde T. Ogunyemi conceptualized and supervised the study, contributed to methodology development, data interpretation, critical revision of the manuscript, and approved the final version for publication.

