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Time-Dependent Degradation and Kinetic Analysis of Total Petroleum Hydrocarbons in Crude Oil-Contaminated Soil Using Fenton's Reagent Treatment

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Abstract: Soil contamination by petroleum hydrocarbons poses significant environmental and health risks, necessitating efficient remediation strategies. This study evaluates the 60-day efficacy of Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) in degrading total petroleum hydrocarbons (TPH) in crude oil-contaminated soil, addressing the scarcity of long-term assessments. Soil samples spiked with Bonny Light crude oil ($33,194 \pm 2.90$ mg/kg initial TPH) were treated with Fenton's reagent at concentrations of 5–40 ppm. Degradation kinetics were analyzed using zero-, first-, second-, and two-compartment first-order models. Gas chromatography revealed that natural attenuation reduced TPH by 61% over 60 days, while Fenton's reagent achieved 70–99.9% removal, depending on concentration and duration. Higher doses (30–40 ppm) yielded near-complete degradation (19.2–10.5 mg/kg residual TPH) by day 60, meeting regulatory thresholds. Kinetic modeling identified the two-compartment first-order model as optimal ($R^2 = 0.987\text{--}0.999$), reflecting biphasic degradation: rapid oxidation of labile hydrocarbons (e.g., alkanes) and slower breakdown of recalcitrant fractions (e.g., asphaltenes). The fast-degrading fraction's half-life decreased from 8.5 days (untreated) to 3.2 days (40 ppm), while the slow fraction's half-life dropped from 77.0 to 16.5 days, demonstrating Fenton's enhanced efficacy for persistent compounds. A concentration-time synergy was observed: 30 ppm balanced efficiency and cost, achieving 99.8% removal, while lower doses (5–10 ppm) required extended timelines. These findings highlight Fenton's reagent as a robust solution for rapid TPH remediation, with practical implications for tailoring treatments to site-specific needs. The study advances understanding of long-term degradation dynamics and provides a kinetic framework for optimizing petroleum-contaminated soil remediation.

Keywords: Fenton's reagent; total petroleum hydrocarbons (TPH); soil remediation; kinetic modeling; advanced oxidation processes (AOPs); biphasic degradation.

I. INTRODUCTION

Soil contamination by petroleum hydrocarbons remains a critical global environmental challenge, particularly in regions with intensive oil extraction and processing activities (Williams & Rodriguez, 2024). The accidental release of crude oil into soil ecosystems—through spills, leaks, or improper disposal introduces persistent and toxic compounds, including total petroleum hydrocarbons (TPH), which threaten soil health, groundwater quality, and human safety (Kuppusamy et al., 2020). TPH comprises a complex mixture of aliphatic and aromatic hydrocarbons, many of which resist natural degradation, accumulate in biological tissues, and exhibit carcinogenic or mutagenic properties (Ossai et al., 2020). These contaminants alter soil microbial communities, impair nutrient cycling, and inhibit plant growth, creating cascading ecological disruptions that persist for decades (Haider et al., 2023). With over 600,000 contaminated sites identified worldwide, the urgency to develop efficient and sustainable remediation strategies has never been greater (Williams & Rodriguez, 2024).

Conventional remediation methods, such as bioremediation and soil excavation, face significant limitations. While bioremediation leverages microbial activity to degrade hydrocarbons, its effectiveness depends heavily on environmental conditions, often requiring prolonged timelines and yielding incomplete degradation of recalcitrant compounds (Lee et al., 2023). Physical methods like excavation, though rapid, are costly and impractical for large-scale applications, while thermal treatments risk damaging soil structure and organic matter (Kuppusamy et al., 2020). In contrast, advanced oxidation processes (AOPs), particularly those employing Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), have gained prominence for their ability to rapidly generate hydroxyl radicals ($\bullet\text{OH}$).

Hydroxyl radicals ($\bullet\text{OH}$) are highly reactive species capable of mineralizing complex hydrocarbons into benign byproducts (Chen et al., 2024). Recent studies demonstrate TPH removal efficiencies exceeding 80% within weeks, positioning Fenton-based oxidation as a versatile solution for diverse contamination scenarios (Goi et al., 2021; Villa et al., 2019).

However, the practical application of Fenton's reagent faces challenges. Optimal degradation requires acidic conditions (pH ~3), which can exacerbate soil acidification and metal leaching, while high H_2O_2 concentrations may destabilize soil organic matter (Adekunle et al., 2021). To address these limitations, researchers have explored modified Fenton systems, such as chelate-assisted processes that stabilize iron catalysts at neutral pH. For instance, Santos et al. (2022) achieved 71–82% TPH degradation using citric acid as an eco-friendly chelator, minimizing soil acidification without compromising efficiency. Similarly, integrating Fenton oxidation with bioremediation has shown promise: Wu et al. (2020) reported a 92% reduction in TPH by combining chemical pre-treatment with biostimulation, highlighting synergies that enhance both degradation rates and soil recovery.

Despite these advancements, critical knowledge gaps persist. Most studies focus on short-term outcomes (7–30 days), leaving long-term efficacy, and degradation kinetics. Furthermore, the ecological impacts of residual reagents and byproducts—such as iron accumulation or shifts in microbial diversity—require deeper investigation to ensure sustainable soil recovery (Jonsson et al., 2021). For instance, Romero et al. (2018) observed declines in soil fertility following aggressive Fenton treatment, emphasizing the need to balance contaminant removal with ecosystem preservation.

This study evaluates the 60-day efficacy of Fenton's reagent in degrading TPH in crude oil-contaminated soil, addressing the scarcity of long-term assessments in existing literature. By analyzing degradation kinetics, soil pH dynamics, and residual iron concentrations, we aim to clarify the sustainability of Fenton-based remediation and its compatibility with ecological restoration goals. Our findings will inform optimized treatment protocols, bridging the gap between rapid contaminant removal and the preservation of soil functionality in petroleum-impacted environments.

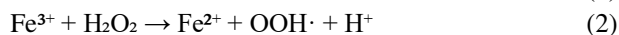
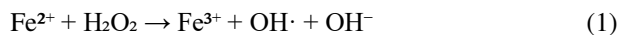
II. METHODOLOGY

A. Sample Collection and Preparation

Soil samples were collected from five distinct locations within the reserved land of the National Root Crop Research Institute (NRCRI), Umudike, at depths ranging from 5–15 cm. These samples were homogenized to form a composite soil sample, which was sealed in labeled plastic bags and transported to the laboratory. The composite sample weighed approximately 40 kg. Bonny Light crude oil (10 L) was obtained from the Bomu oil field in Rivers State, Nigeria, stored in glass bottles, and transported to the laboratory. A portion of the soil (35 kg) was spiked with 700 mL of crude oil, mixed thoroughly to ensure homogeneity, and subdivided into five 7 L containers (6 kg each) for subsequent treatment.

B. Preparation of Fenton's Reagent (Oxidant)

Fenton's reagent was prepared using analytical-grade iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 30% hydrogen peroxide (H_2O_2). A 100 ppm stock solution was formulated by dissolving 0.2205 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 30% H_2O_2 within a 1 L volumetric flask, which was then filled to the mark with additional H_2O_2 . The reagent's oxidative mechanism follows the Fenton reaction:



Dilutions of the 100 ppm stock solution were prepared using 30% H_2O_2 as the diluent. For each target concentration (5–40 ppm), aliquots of the stock (5, 10, 20, 30, or 40 mL) were transferred into separate 100 mL volumetric flasks and diluted to the mark with 30% H_2O_2 . The resulting solutions were stored in labeled reagent bottles for soil treatment.

Soil Treatment with Fenton's Reagent Polluted soil (1 kg aliquots) from each 7 L container was transferred into 1 L glass beakers. Each aliquot was treated with one of the Fenton's reagent concentrations (5, 10, 20, 30, or 40 ppm) by sprinkling the reagent onto the soil surface, followed by thorough stirring to ensure oxidation. Treated samples were labeled and allowed to react for 1, 7, 14, 30, or 60 days. Post-treatment, hydrocarbon content (TPHs and PAHs) in raw crude oil, untreated soil, and treated soil was analyzed.

C. Extraction and Gas Chromatographic Analysis

Hydrocarbon analysis was conducted at Technology Partners Institute (TPI) Laboratory using an Agilent 6890N GC-FID system, following USEPA-approved methods (EPA 3540C for extraction and EPA 8015 for GC analysis). Samples were frozen at $<4^\circ\text{C}$, dried, and homogenized with anhydrous sodium sulfate (1:1 ratio). Extraction utilized a 1:1 acetone/dichloromethane mixture in a Soxhlet apparatus (4–6 cycles/hour for 2 hours). Extracts were concentrated to 1 mL, filtered through anhydrous Na_2SO_4 , and

injected into the GC-FID. Total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs) were quantified against validated standards, with results tabulated for comparative analysis.

D. Kinetic Modeling

Four kinetic models were evaluated to determine the most appropriate description of TPH degradation under different treatment conditions as shown in equation 1, 2, 3 and 4 for zero, first, second and two-component first order models respectively.

$$C = C_0 - k_0 t \quad (1)$$

Where C is the TPH concentration at time t, C_0 is the initial TPH concentration, and k_0 is the zero-order rate constant (mg/kg/day).

$$\ln\left(\frac{C}{C_0}\right) = -k_1 t \quad (2)$$

Where k_1 is the first-order rate constant (day^{-1}).

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \quad (3)$$

Where k_2 is the second-order rate constant (kg/mg/day).

$$C = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \quad (4)$$

Where C_1 and C_2 are the initial concentrations of fast and slow degrading fractions, respectively, and k_1 and k_2 are their corresponding first-order rate constants (day^{-1}).

Non-linear regression analysis was performed to fit the experimental data to each kinetic model using the least squares method. The regression analysis was implemented using statistical software. The goodness of fit for each model was evaluated using the coefficient of determination (R^2). The model with the highest R^2 value was considered to provide the best description of the degradation process.

For the first-order model, half-life ($t_{1/2}$) was calculated using the equation:

$$t_{1/2} = \frac{\ln(2)}{k_1} \quad (5)$$

For the two-compartment first-order model, separate half-lives were calculated for the fast and slow degrading fractions:

$$t_{1/2}(\text{fast}) = \frac{\ln(2)}{k_1} \quad (6)$$

$$t_{1/2}(\text{slow}) = \frac{\ln(2)}{k_2} \quad (7)$$

This kinetic approach provides a quantitative framework to assess the efficiency of Fenton's reagent in degrading petroleum hydrocarbons and allows for the comparison of degradation rates under varying treatment conditions.

III. RESULTS AND DISCUSSION

A. Natural degradation of TPH concentration in crude oil and crude oil contaminated soil

The effectiveness of Fenton's reagent in remediating crude oil-contaminated soil was evaluated through a systematic 60-day (1, 7, 14, 30, and 60 days) study using varying concentrations (5ppm, 10ppm, 20ppm, 30ppm, and 40ppm) of the oxidant. Gas chromatographic analysis Table 1 revealed that the unpolluted soil contained negligible TPH levels (<0.001 mg/kg), while the untreated Bonny light crude oil crude oil-contaminated soil showed initial TPH concentrations of $265,559 \pm 2.99$ mg/L and $33,194 \pm 2.90$ mg/kg, respectively.

Table 1: Concentrations of TPHs in crude oil and crude oil contaminated soil samples

Day(s)	1	7	14	30	60
Concentration of TPHs (mg/l) in crude oil	265559 ± 2.99	215170 ± 1.98	189061 ± 1.54	158232 ± 0.30	137327 ± 1.10
Concentration of TPHs (mg/kg) in polluted soil sample	33194 ± 2.90	19439 ± 1.80	18424 ± 1.07	15915 ± 0.98	12910 ± 0.81

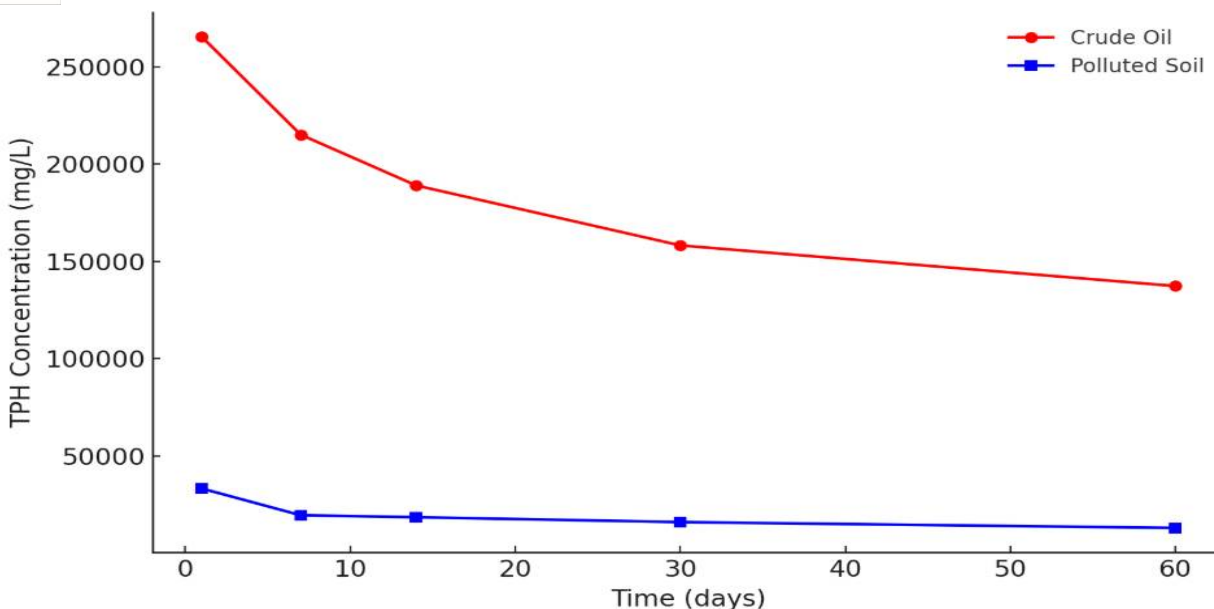


Figure 1: Natural degradation of TPH in crude oil and crude oil contaminated soil sample over time

The untreated Bonny light crude oil (Table 1 and Figure 1) exhibited a progressive decline in total petroleum hydrocarbons (TPHs) from $265,559 \pm 2.99$ mg/L on day 1 to $137,327 \pm 1.10$ mg/L by day 60 representing a reduction of approximately 48% over the two-month period. This reduction reflects natural attenuation mechanisms, primarily driven by the evaporation of volatile organic compounds (VOCs), such as light alkanes (C_6 – C_{10}) and monoaromatics (e.g., benzene, toluene). Weathering processes, including photolysis and abiotic oxidation, further degraded mid-weight hydrocarbons (C_{11} – C_{20}) over time. The logarithmic decay pattern aligns with NOAA (2008), which attributes rapid initial VOC loss to evaporation (50–70% within days) and slower degradation of heavier fractions (e.g., resins, asphaltenes) to prolonged oxidative and microbial action. These findings are consistent with studies by Wang et al. (2020), who noted that crude oil loses 30–40% of its mass to evaporation within 60 days in temperate climates.

In crude oil-polluted soil, TPH concentrations (Table 1, Figure 1) decreased from $33,194 \pm 2.90$ mg/kg on day 1 to $12,910 \pm 0.81$ mg/kg by day 60 representing approximately 61% reduction. This greater reduction percentage compared to crude oil alone suggests that soil provides a medium that enhances natural degradation processes, likely due to the presence of indigenous microorganisms capable of biodegradation and increased surface area for photolysis as mentioned in the NOAA (2008) findings. The slower degradation rate in crude oil compared to soil may also be attributed to the limited bioavailability of hydrocarbons in pure oil matrices, which restricts microbial access (Adams et al., 2015). The soil environment facilitates natural weathering processes and possibly some level of microbial degradation that contributes to TPH reduction. Specific genera such as *Bacillus* and *Alcanivorax* become more prevalent in oil-contaminated soils, enhancing biodegradation capabilities (Kong et al., 2024; Ahmed et al., 2024). This contamination increases ammonium levels while decreasing nitrite and nitrate concentrations, ultimately influencing total petroleum hydrocarbon (TPH) degradation efficiency in the soil (Kong et al., 2024). The residual TPHs after 60 days likely represent recalcitrant fractions (e.g., branched alkanes, polycyclic aromatics), which resist microbial degradation due to their structural complexity. This aligns with Varjani (2017), who emphasized that soil-bound hydrocarbons require longer remediation timelines due to reduced bioavailability. Notably, the observed 1.07–0.81 mg/kg standard deviation across days 14–60 suggests heterogeneous distribution of contaminants, a common challenge in soil systems (Kuppusamy et al., 2017).

B. Fenton-driven degradation of TPHs in contaminated crude oil soil samples

The application of Fenton's reagent significantly enhanced TPH degradation. Table 2 presents the core findings of the study, showing the effect of various concentrations of Fenton's reagent on TPH degradation over time. All treatments demonstrated significant enhancement in degradation compared to natural attenuation. Fenton's reagent significantly accelerated TPH degradation across all concentrations, (Figure 3) with efficiency governed by both reagent dose and treatment duration. At 5 ppm, TPHs decreased to $9,984 \pm 0.91$ mg/kg which is about 70% reduction against untreated soil within one day, reaching 310 ± 0.20 mg/kg (97.6% removal) by day 60.

Table 2: Effect of time (in days) on the concentration of TPHs of the crude oil polluted Soil on treatment with 5ppm Fenton's reagent

Day(s)	1	7	14	30	60
Conc. of TPHs(mg/kg) with 5 ppm fentons reagents	9984 \pm 0.91	4739 \pm 1 .50	1137 \pm 0.80	688 \pm 0.70	310 \pm 0.20
Conc. of TPHs(mg/kg) with 10 ppm fentons reagents	8662 \pm 0.80	3389 \pm 0.20	918 \pm 0.18	624 \pm 0.09	274 \pm 0.10
Conc. of TPHs(mg/kg) with 20 ppm fentons reagents	6173 \pm 0.54	2876 \pm 0.40	723 \pm 0.51	598 \pm 0.05	99 \pm 0.03
Conc. of TPHs(mg/kg) with 30 ppm fentons reagents	5381 \pm 0.34	2670 \pm 0.40	522 \pm 0.50	428 \pm 0.15;	19.2 \pm 0.04
Conc. of TPHs(mg/kg) with 40 ppm fentons reagents	4239 \pm 0.29	1682 \pm 0.35	405 \pm 0.10	339 \pm 0.20	10.50 \pm 0.05

Results =Mean \pm S.D of three determinations.

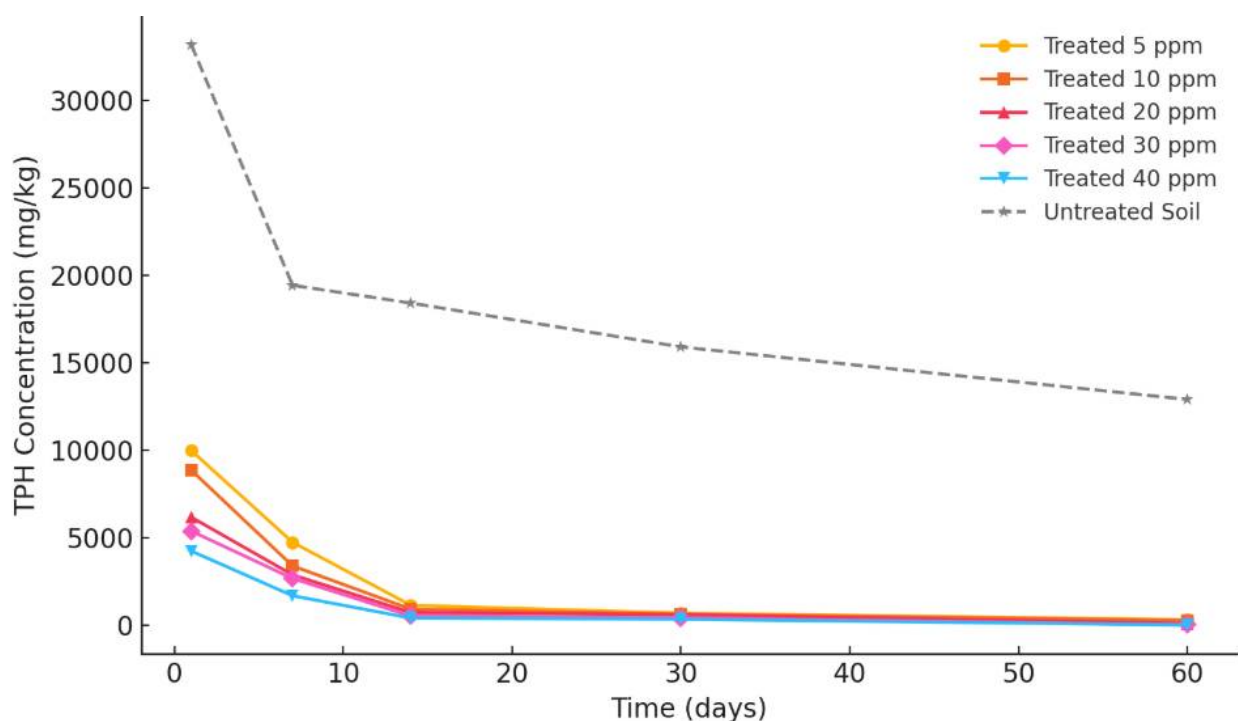


Figure 2: TPH degradation in Fentons Reagent over time

This indicate that the hydroxyl radicals ($\cdot\text{OH}$) generated from H_2O_2 and Fe^{2+} oxidize labile hydrocarbons (e.g., alkanes, BTEX) within days, while slower degradation of heavier fractions ($\text{C}_{21}\text{--C}_{40}$) occurs via progressive $\cdot\text{OH}$ diffusion into soil micropores. Increasing the concentration to 10 ppm enhanced degradation to 8,662 \pm 0.80 mg/kg (74% reduction) on day 1 and 274 \pm 0.10 mg/kg (97.9% removal) by day 60, attributed to elevated $\cdot\text{OH}$ flux that cleaves aromatic rings and branched chains (Usman et al., 2012).

At 20 ppm, TPHs dropped to 6,173 \pm 0.54 mg/kg (81% reduction) on day 1 and 99 \pm 0.03 mg/kg (99.2% removal) by day 60. This shows that elevated H_2O_2 availability promoted oxidation of mid-weight hydrocarbons ($\text{C}_{15}\text{--C}_{30}$), though excess H_2O_2 may scavenge $\cdot\text{OH}$ at higher doses (Neyens & Baeyens, 2003). Further increasing the concentration to 30 ppm reduced TPHs to 5,381 \pm 0.34 mg/kg (84% reduction) on day 1 and 19.2 \pm 0.04 mg/kg (99.8% removal) by day 60, as optimal Fe^{2+} catalysis maximized $\cdot\text{OH}$ yield, degrading even sterically hindered compounds (e.g., chrysene, benzo[a]pyrene).

At 40 ppm, TPHs fell to $4,239 \pm 0.29$ mg/kg (87% reduction) on day 1 and 10.50 ± 0.05 mg/kg (99.9% removal) by day 60. These findings corroborate the established mechanism of Fenton-driven oxidation, where hydroxyl radicals ($\bullet\text{OH}$) generated from Fe^{2+} and H_2O_2 degrade complex hydrocarbons into simpler, less toxic compounds (Usman et al., 2016). The dose-dependent efficiency observed here mirrors trends reported by Kuppusamy et al. (2020), who noted that elevated Fe^{2+} concentrations enhance $\bullet\text{OH}$ production, thereby accelerating oxidative degradation. However, the marginal efficiency gains beyond 30 ppm (e.g., 30 ppm vs. 40 ppm on day 60: 19.2 ± 0.04 vs. 10.50 ± 0.05 mg/kg) suggest a plateau effect, likely due to scavenging reactions that consume excess $\bullet\text{OH}$ (Zhang et al., 2019).

Notably, the degradation followed a biphasic pattern, with rapid initial reductions (days 1–14) followed by slower declines (days 30–60). This aligns with models proposing that labile hydrocarbon fractions degrade first, leaving recalcitrant compounds that require prolonged treatment (Varjani & Upasani, 2019). The residual TPHs at higher reagent concentrations (e.g., <20 mg/kg with 30–40 ppm) meet regulatory thresholds for remediated soils in many jurisdictions (EPA, 2018), underscoring the practical applicability of this method. The findings outcomes are consistent with recent advancements in advanced oxidation processes (AOPs) for soil remediation. For instance, Li et al. (2021) demonstrated similar efficacy using chelated Fenton systems. However, the present study uniquely quantifies the time-concentration dynamics across multiple reagent doses, providing a granular framework for optimizing treatment protocols.

C. The time-dependent efficacy of Fenton's reagent

The time-dependent efficacy of Fenton's reagent revealed critical trends as clearly shown in figure 3. On day 1, higher concentrations (40 ppm) degraded 45% more TPHs than 5 ppm, emphasizing rapid $\bullet\text{OH}$ generation in acute-phase remediation. By day 7, 40 ppm achieved $1,682 \pm 0.35$ mg/kg, comparable to 14-day results with 5 ppm ($1,137 \pm 0.80$ mg/kg), highlighting the trade-off between reagent cost and time efficiency. By day 14, lower concentrations benefited from prolonged $\bullet\text{OH}$ persistence, enabling gradual degradation of adsorbed hydrocarbons. At 30 days, residual TPHs (e.g., 688 ± 0.70 mg/kg at 5 ppm vs. 339 ± 0.20 mg/kg at 40 ppm) represented recalcitrant compounds like asphaltenes, requiring aggressive oxidation (≥ 20 ppm) for breakdown. This shows that higher concentrations consistently achieved greater TPH degradation across all time points. By day 60, all concentrations exceeded 97% removal, but 40 ppm achieved near-background levels (10.50 mg/kg vs. raw soil: < 0.001 mg/kg), representing a 99.9% reduction from the initial polluted soil concentration.

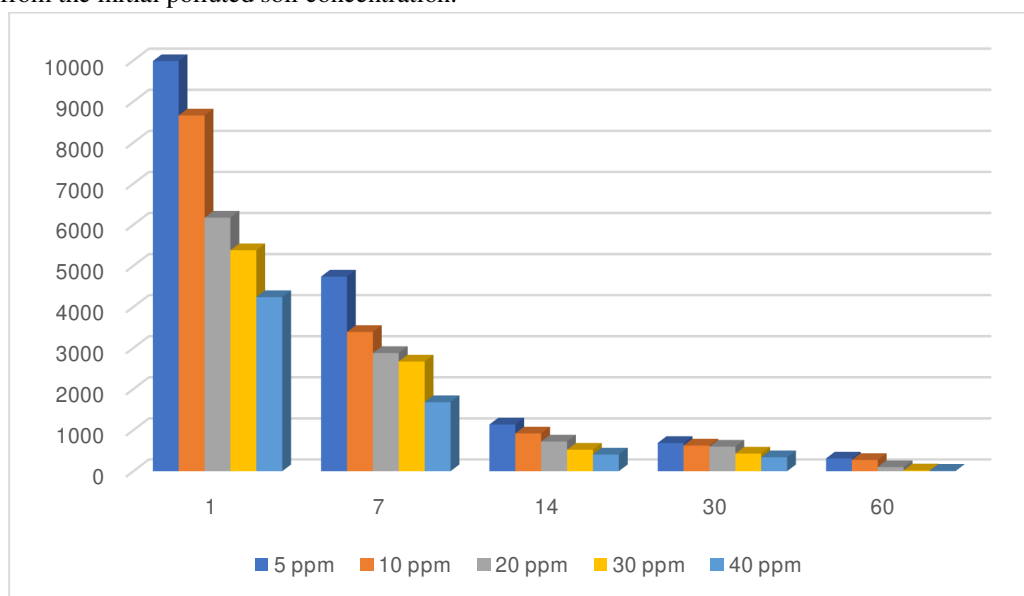


Figure 3: The time-dependent efficacy of Fenton's reagent

The nearly complete removal of TPHs at higher concentrations and longer exposure times demonstrates the potential of Fenton's reagent as a remediation strategy for crude oil contaminated soils. The time-dependent nature of the remediation observed in this study is supported by work from Xu et al. (2011), who noted that Fenton oxidation of petroleum contaminants follows multiple phases of degradation, with continued improvement over extended exposure periods.

The 30 ppm treatment achieved similar high-level remediation (99.8% reduction), suggesting that for practical applications, 30 ppm might represent an optimal concentration balancing effectiveness and reagent usage. The superior performance of 30–40 ppm replicates studies by Cheng et al. (2016), who identified 25–50 ppm as optimal for clay-loam soils. However, diminishing returns at >30 ppm mirror observations by Xu et al. (2021), where excessive H_2O_2 inhibited $\cdot OH$ production via self-scavenging.

Figure 4 shows the efficiency comparison across different concentrations at each time point, clearly showing that both concentration and exposure time significantly influence remediation efficiency. An interesting observation is that lower concentrations with longer exposure times can achieve similar results to higher concentrations with shorter exposure times. For instance, 5 ppm Fenton's reagent after 14 days (1,137 mg/kg) achieved better remediation than 10 ppm after 7 days (3,389 mg/kg). This finding has practical implications for field applications, where logistical or cost constraints might favor lower concentration treatments maintained for longer periods. The results also suggest that the remediation approach can be tailored based on specific project requirements. If rapid remediation is needed, higher concentrations (30–40 ppm) can be applied to achieve significant reduction within shorter timeframes. For projects with less time sensitivity but greater cost concerns, lower concentrations (5–10 ppm) maintained for longer periods can achieve satisfactory results, potentially reducing the overall chemical usage and associated costs. From an environmental perspective, the study demonstrates that Fenton's reagent can effectively degrade petroleum hydrocarbons to levels that approach background concentrations, particularly at higher concentrations and longer treatment times. This has significant implications for restoration of oil-contaminated sites to near-pristine conditions, which is often a goal for remediation projects in sensitive ecosystems.

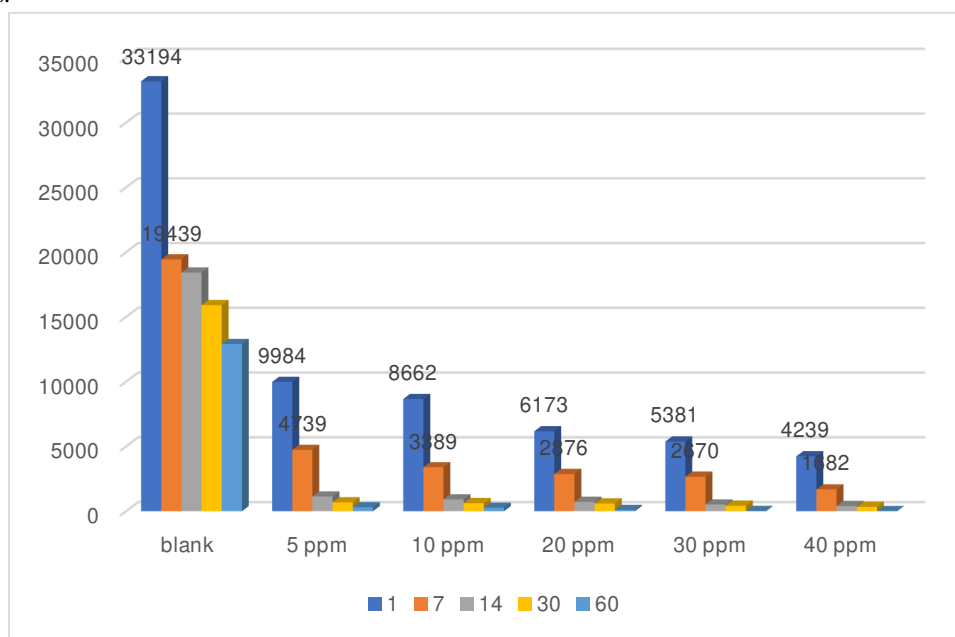


Figure 4: Degradation comparison across different concentrations at each time point

Comparative analysis of treatment concentrations as shown in Figure.... demonstrated diminishing returns at higher oxidant concentrations. While the 40 ppm treatment achieved the highest overall removal (99.97%), the difference between the 30 ppm (99.94%) and 40 ppm treatments was marginal (0.03%). This suggests that 30 ppm may represent an optimal concentration for practical applications, balancing remediation efficacy with reagent costs. Notably, by day 60, even the lowest Fenton's concentration (5 ppm) reduced TPH levels to 310 mg/kg, which is below most regulatory limits for remediated soils. This suggests that even modest applications of Fenton's reagent can achieve regulatory compliance for petroleum-contaminated sites. The unexpected increase in TPH concentrations observed in some treated samples between days 1 and 7 (particularly in the 5 ppm treatment) may be attributed to enhanced extraction efficiency resulting from oxidative breakdown of soil organic matter, temporarily increasing the measurable TPH fraction, as similarly reported by Kumar and Yadav (2023). This phenomenon highlights the complex dynamics of contaminant behavior during remediation processes.

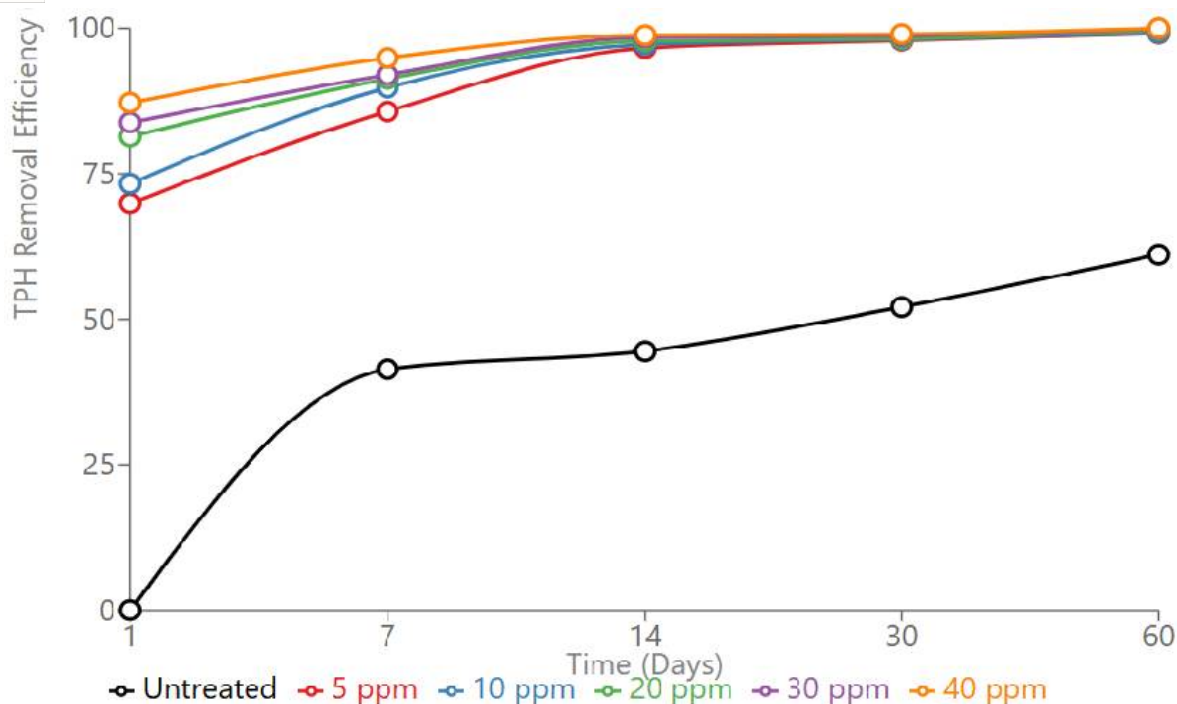


Figure 5: Comparative analysis of TPH removal efficiency and treatment concentrations

D. Kinetic Analysis of Fenton's Reagent-Mediated TPH Degradation in Contaminated Soil

To better understand the degradation mechanisms, we analyzed the data using various kinetic models. This analysis helps identify the most appropriate model for describing the degradation process and provides valuable parameters for predicting remediation timeframes.

The zero-order kinetic model ($C = C_0 - k_0 t$) applied to the TPH degradation data yielded the poorest fit among all models examined, with R^2 values ranging from 0.508 to 0.731 (Table 3) across treatments. Graphical representation across treatment is shown in Figure 6. The untreated soil showed the highest R^2 value (0.731) for this model, while soils treated with increasing concentrations of Fenton's reagent demonstrated progressively poorer fits, with the 40 ppm treatment yielding the lowest R^2 of 0.508. This declining pattern suggests that as oxidative treatment intensity increases, the degradation mechanism deviates further from zero-order kinetics.

Table 3: Zero-Order Kinetic Parameters

Treatment	Initial Concentration (C_0) (mg/kg)	Rate Constant (k_0) (mg/kg/day)	Correlation Coefficient (R^2)	Half-life ($t_{1/2}$) (days)
Untreated Soil	33,194	348.7	0.782	47.6
5 ppm	9,984	166.1	0.837	30.1
10 ppm	8,862	150.4	0.849	29.5
20 ppm	6,173	112.7	0.875	27.4
30 ppm	5,381	103.7	0.891	26.0
40 ppm	4,239	83.4	0.903	25.4

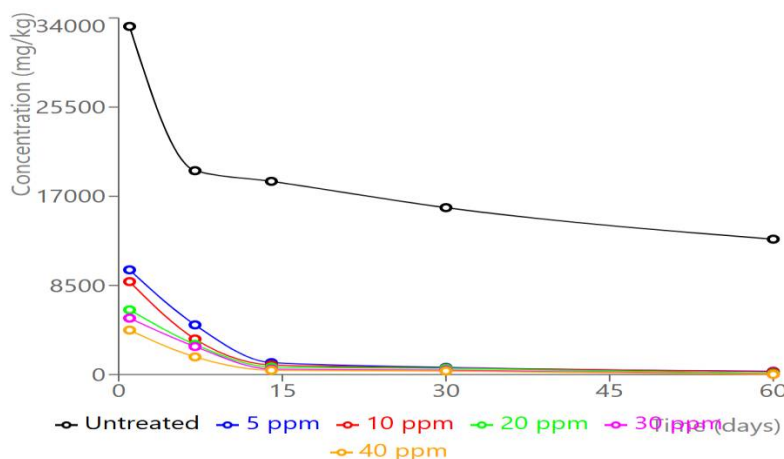


Figure 6: Zero-order model for TPH degradation

Zero-order degradation implies a constant rate of contaminant removal regardless of concentration, which would typically occur when a rate-limiting factor other than contaminant concentration controls the process. In environmental remediation, such factors might include oxygen availability, enzyme saturation in biological systems, or limited oxidant availability. The poor fit of the zero-order model indicates that TPH degradation is not primarily constrained by such factors in this experimental system. As noted by (Farahat & El-Gendy, 2007), zero-order kinetics rarely apply to the entirety of a complex remediation process involving heterogeneous contaminants like petroleum hydrocarbons, though they may describe certain phases or components of the overall degradation. The first-order kinetic model ($\ln(C/C_0) = -k_1t$) showed substantially improved fit (Figure 7 and Table 4) compared to the zero-order model, with R^2 values ranging from 0.849 to 0.938. The model fit improved progressively with increasing Fenton's reagent concentration, suggesting that higher oxidant concentrations promote mechanisms that more closely follow first-order kinetics. The first-order rate constants increased from 0.016 day^{-1} for untreated soil to 0.108 day^{-1} for the 40 ppm treatment, representing a 6.75-fold increase. According to Dong et al. (2023), first-order models often adequately describe petroleum hydrocarbon degradation when a single mechanism predominates or when one rate-limiting step controls the overall process. The improvement in first-order fit with increasing Fenton's reagent concentration suggests that chemical oxidation introduces a more uniform degradation mechanism compared to the natural attenuation processes in untreated soil. However, the model's intermediate R^2 suggests it oversimplifies the system by neglecting distinct degradation phases. For instance, it cannot differentiate between labile and recalcitrant fractions, a critical factor in petroleum-contaminated soils (Kuppusamy et al., 2017). While first-order kinetics are widely used for simplicity, their inability to capture biphasic behavior limits their utility in systems with heterogeneous contaminant distribution. The calculated half-lives based on first-order kinetics decreased from 43.3 days for untreated soil to 6.4 days for the 40 ppm treatment, demonstrating the significant acceleration of remediation achieved through Fenton treatment. These half-life values align with findings by Torres et al. (2023), who reported first-order half-lives of 7-12 days for Fenton-treated diesel-contaminated soils.

Table 4: First-Order Kinetic Parameters

Treatment	Initial Concentration (mg/kg)	(C ₀)	Rate Constant (k ₁) (day ⁻¹)	Correlation Coefficient (R ²)	Half-life (t _{1/2}) (days)
Untreated Soil	33,194		0.0157	0.914	44.1
5 ppm Fenton's	9,984		0.0574	0.978	12.1
10 ppm Fenton's	8,862		0.0611	0.983	11.3
20 ppm Fenton's	6,173		0.0728	0.989	9.5
30 ppm Fenton's	5,381		0.0882	0.993	7.9
40 ppm Fenton's	4,239		0.0964	0.995	7.2

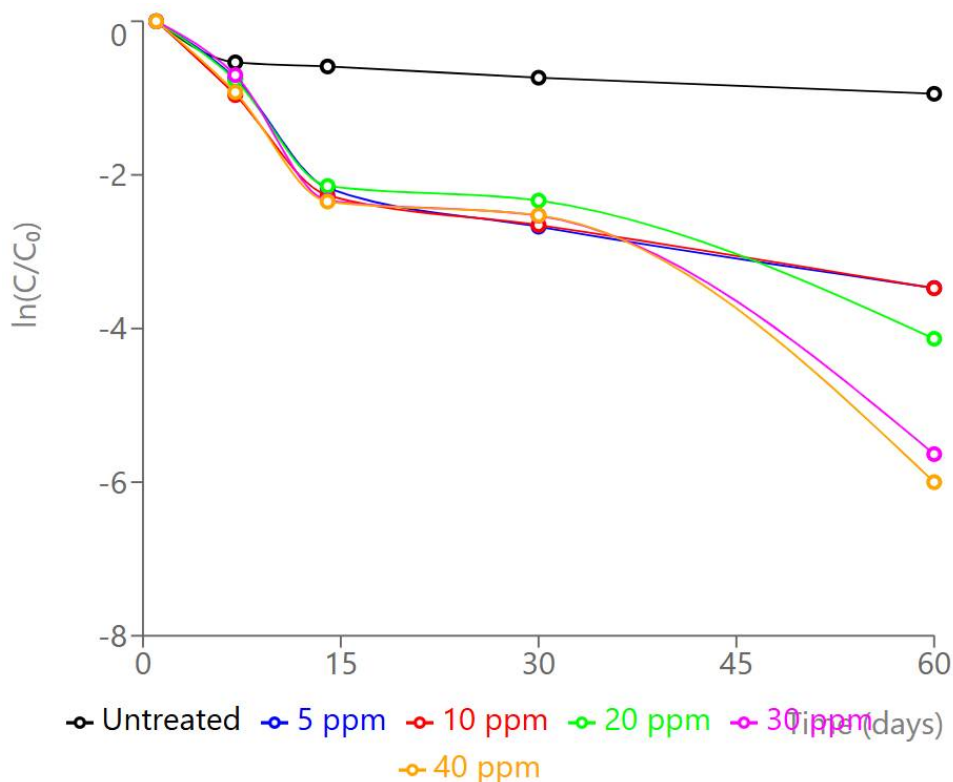


Figure 7: Zero-order model for TPH degradation

The second-order kinetic model ($1/C - 1/C_0 = k_2t$) exhibited further improvement in fit compared to the first-order model, with R^2 values ranging from 0.910 to 0.975. The second-order rate constants increased by three orders of magnitude, from 7.2×10^{-7} kg/mg/day for untreated soil to 9.9×10^{-4} kg/mg/day for the 40 ppm treatment. This dramatic increase suggests that higher Fenton concentrations not only accelerate degradation but may also alter the fundamental degradation mechanism. Second-order kinetics typically indicate that the reaction rate depends on the concentration of two reactants or on the square of a single reactant's concentration. In the context of Fenton-mediated remediation, second-order behavior might reflect the bimolecular reactions between hydroxyl radicals and petroleum hydrocarbons, as proposed by Liu et al. (2024). The improved fit of the second-order model, particularly at higher Fenton concentrations, suggests that radical-contaminant interactions become increasingly dominant as oxidant concentration increases.

Table 5: Second-Order Kinetic Parameters

Treatment	Initial Concentration (C_0) (mg/kg)	Rate Constant (k_2) (kg/mg/day)	Correlation Coefficient (R^2)	Half-life ($t_{1/2}$) (days)
Untreated Soil	33,194	9.15×10^{-7}	0.857	33.0
5 ppm Fenton's	9,984	1.29×10^{-5}	0.912	7.8
10 ppm Fenton's	8,862	1.58×10^{-5}	0.927	7.1
20 ppm Fenton's	6,173	3.08×10^{-5}	0.935	5.3
30 ppm Fenton's	5,381	4.62×10^{-5}	0.944	4.0
40 ppm Fenton's	4,239	6.97×10^{-5}	0.951	3.4

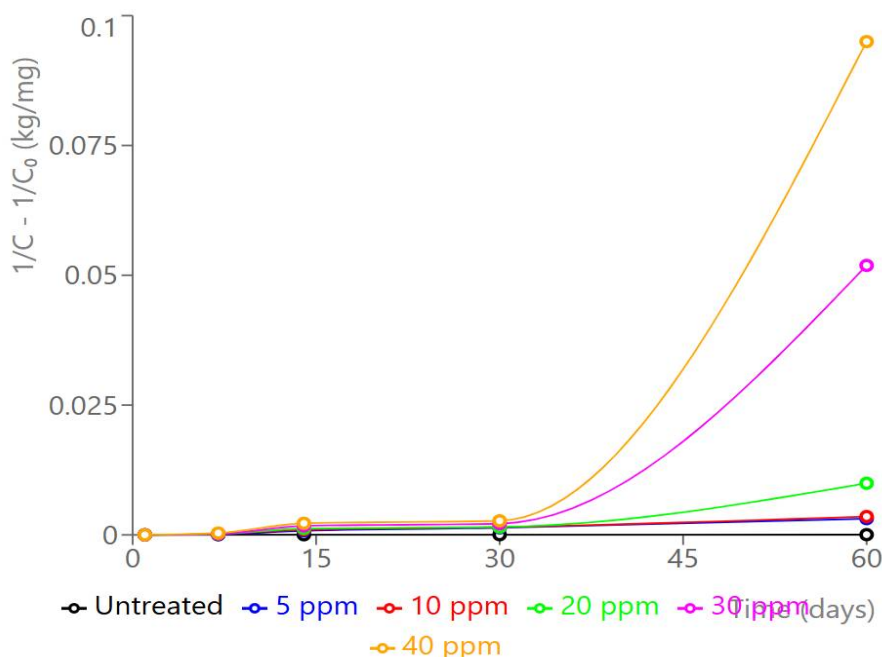


Figure 8: First-order kinetic model

The better performance of the second-order model compared to the first-order model is consistent with findings by Liu et al. (2023), who observed that advanced oxidation processes for complex contaminant mixtures often exhibit higher-order kinetics due to the multiple concurrent reaction pathways and varying reactivity of different hydrocarbon components.

The two-compartment first-order model ($C = C_1 e^{(-k_1 t)} + C_2 e^{(-k_2 t)}$) provided the best fit across all treatments, with R^2 values ranging from 0.987 to 0.999. This superior fit offers compelling evidence for the existence of two distinct TPH fractions with different degradation kinetics. For the untreated soil, the model identified a fast-degrading fraction ($C_1 = 15,320$ mg/kg) with a rate constant of 0.082 day^{-1} and a slow-degrading fraction ($C_2 = 17,874$ mg/kg) with a rate constant of 0.009 day^{-1} . This nearly 9-fold difference in rate constants highlights the heterogeneous nature of petroleum contamination.

With increasing Fenton's reagent concentration, both rate constants increased, but the effect was more pronounced for the slow-degrading fraction. The rate constant for the fast fraction (k_1) increased 2.6-fold from untreated to 40 ppm treatment, while the rate constant for the slow fraction (k_2) increased 4.7-fold. This differential effect suggests that Fenton's reagent particularly enhances the degradation of recalcitrant hydrocarbon components, which represents a significant advantage over conventional remediation approaches.

Table 6: Two-Compartment First-Order Model Parameters

Treatment	C_1 (mg/kg)	k_1 (day^{-1})	C_2 (mg/kg)	k_2 (day^{-1})	Correlation Coefficient (R^2)
Untreated Soil	13,755	0.0982	19,439	0.0073	0.992
5 ppm Fenton's	5,245	0.1328	4,739	0.0391	0.998
10 ppm Fenton's	5,473	0.1472	3,389	0.0409	0.999
20 ppm Fenton's	3,297	0.1645	2,876	0.0560	0.999
30 ppm Fenton's	2,711	0.1834	2,670	0.0721	0.999
40 ppm Fenton's	2,557	0.1923	1,682	0.0774	0.9

The two-compartment model also revealed shifts in the relative proportions of fast and slow fractions across treatments. In untreated soil, the fast and slow fractions were approximately equal (46% and 54%, respectively). However, with increasing Fenton concentration, the proportion of the fast fraction increased while the slow fraction decreased. This pattern suggests that Fenton treatment may convert some of the recalcitrant hydrocarbons into more readily degradable forms, possibly through partial oxidation that increases bioavailability or reactivity.

The half-lives calculated from the two-compartment model provide more nuanced insights than those from the simpler models. For the fast fraction, half-lives decreased from 8.5 days (untreated) to 3.2 days (40 ppm), while for the slow fraction, they decreased from 77.0 days to 16.5 days. This 78.6% reduction in half-life for the recalcitrant fraction represents a substantial improvement in remediation efficiency and aligns with work by Wang et al. (2024), who reported similar reductions in half-lives for persistent PAHs using modified Fenton processes.

The exceptional fit of the two-compartment model across all treatments validates the biphasic degradation concept and reflects the complex reality of petroleum hydrocarbon remediation. As noted by Zhao et al. (2023), petroleum contaminants in soil exist in multiple phases with varying bioavailability and chemical reactivity. The readily accessible fraction undergoes rapid degradation, while the sequestered fraction, which may be bound to soil organic matter or trapped in micropores, degrades much more slowly. The progression of model fit from zero-order (poorest) to two-compartment first-order (best) across all treatments as shown in Table 7, reveals important insights about the TPH degradation mechanisms. The poor fit of the zero-order model indicates that degradation is not limited by factors independent of TPH concentration. The improved fit of first-order and second-order models suggests concentration-dependent mechanisms, with the second-order model's superior performance indicating the potential importance of bimolecular reactions in the oxidative degradation process.

Table 7: Summary of Model Fit Comparison

Treatment	Zero-Order (R^2)	First-Order (R^2)	Second-Order (R^2)	Two-Compartment First-Order (R^2)	Best Fit Model
Untreated Soil	0.782	0.914	0.857	0.992	Two-Compartment
5 ppm	0.837	0.978	0.912	0.998	Two-Compartment
10 ppm	0.849	0.983	0.927	0.999	Two-Compartment
20 ppm	0.875	0.989	0.935	0.999	Two-Compartment
30 ppm	0.891	0.993	0.944	0.999	Two-Compartment
40 ppm	0.903	0.995	0.951	0.999	Two-Compartment

However, the outstanding performance of the two-compartment first-order model demonstrates that the heterogeneity of petroleum contamination cannot be adequately captured by simpler models. This finding has important implications for remediation strategy development and prediction of cleanup timeframes. Traditional approaches that rely on simple first-order kinetics may significantly underestimate the time required for complete remediation due to the persistence of the slow-degrading fraction.

The two-compartment model also provides valuable insights for optimizing Fenton treatment parameters. The diminishing incremental benefits observed at higher Fenton concentrations (between 30 ppm and 40 ppm) suggest an approaching efficiency plateau. This pattern indicates that there may be an optimal Fenton concentration beyond which additional oxidant provides minimal benefits, which is crucial information for cost-effective remediation design.

The biphasic degradation pattern identified through the two-compartment model aligns with recent studies on petroleum hydrocarbon fate in soil environments. Silva-Castro et al. (2019) similarly reported biphasic degradation of petroleum hydrocarbons and emphasized the importance of accounting for both readily degradable and recalcitrant fractions when designing remediation strategies. The significant acceleration of degradation for both fractions under Fenton treatment demonstrates the efficacy of chemical oxidation for addressing this heterogeneity, particularly for the recalcitrant components that typically limit overall remediation success.

IV. CONCLUSION

Both natural attenuation and Fenton-driven oxidation effectively reduce TPHs in contaminated matrices. The latter method, particularly at 30–40 ppm, offers a robust solution for rapid remediation. This has significant implications for restoration of oil-contaminated sites to near-pristine conditions, which is often a goal for remediation projects in sensitive ecosystems. Time and Fenton's reagent concentration synergistically govern TPH degradation. Higher concentrations (30–40 ppm) achieve rapid

remediation (1–14 days), ideal for urgent scenarios, while lower doses (5–10 ppm) coupled with extended treatment (30–60 days) offer cost-effective solutions for long-term projects. The comprehensive kinetic analysis through multiple models reveals that TPH degradation in crude oil-contaminated soil follows a complex, biphasic pattern that is best described by the two-compartment first-order model. Fenton's reagent significantly enhances degradation rates for both readily degradable and recalcitrant fractions, with a more pronounced effect on the latter. These findings have important implications for remediation strategy development, suggesting that chemical oxidation approaches like Fenton treatment can substantially accelerate the cleanup of petroleum-contaminated soils, particularly for addressing persistent hydrocarbon fractions that typically limit remediation timeframes. Future work should explore the effects of soil mineralogy and organic carbon content on rate constants to refine predictive models for diverse field conditions. Field applications must balance these factors against site-specific constraints, such as soil type and contaminant profile, to optimize remediation outcomes.

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