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Effect of Cobalt-Catalysed Persulphate at Varying Concentrations for the Remediation of Petroleum Hydrocarbons in Oil-Contaminated Soil

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ABSTRACT

The indiscriminate discharge of spent lubrication oil into the environment poses health and socio economic risks due to its persistent. This study evaluated the effectiveness of persulphate oxidation in the remediation of soils artificially contaminated with spent lubrication oil. Contamination was performed at a ratio of 1kg of soil: 100 mL of spent lubrication oil. The degradation efficiency of spent lubrication oil was monitored over a six-week treatment period. Results revealed that 0.25 M persulphate without cobalt activation achieved the highest degradation efficiency (88.9%), indicating that sulphate radicals mediated oxidation under ambient soil conditions. Although cobalt activation enhanced initial oxidation rates at higher persulphate dosages, excessive oxidant and cobalt ion concentrations did not yield proportionate improvements in degradation, likely due to radical scarvenging and secondary ion accumulation. On the other hand, the highest natural degradation occurred at 0.1 M persulfate control (13.6%) which may be due to biological variability and possible volatilization of lighter fractions. These results confirmed that persulphate-based oxidation can efficiently degrade petroleum hydrocarbons in oil contaminated soils. However, sequential oxidant application and optimization of soil conditions are recommended to maximize hydrocarbon degradation and minimize negative environmental impact.

Keywords: Batch experiments, cobalt activation, in situ chemical oxidation persulphate oxidation, petroleum hydrocarbon, soil remediation.

INTRODUCTION

The indiscriminate discharge of spent lubrication oil into terrestrial environments represents a significant and persistent environmental challenge, particularly in developing regions. This is composed of chain aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), heavy metals, and degradation additives that are highly resistant to natural attenuation processes [1].

Once released into soil matrices, these contaminants reduce soil fertility, impair microbial activity, and pose serious risks to groundwater quality and human health due to their toxicity, mutagenicity, and persistence [2].

Conventional remediation techniques such as excavation, landfilling, and bioremediation have shown limited success in treating spent lubrication oil-contaminated soils. Physical removal methods are often cost intensive and environmentally disruptive, while biological approaches are constrained by the low bioavailability and recalcitrant nature of heavy petroleum fractions [3]. Consequently, there is increasing interest in *in situ* chemical oxidation (ISCO) as a rapid and effective alternative for degrading petroleum hydrocarbons in contaminated soils [4]. Among ISCO agents, persulphate ($S_2O_8^{2-}$) has emerged as a promising oxidant due to its high stability, ease of handling, and ability to generate powerful sulphate radicals ($SO_4^{\cdot-}$) upon activation [5]. Sulphate radicals possess a high redox potential (2.5-3.1 V), comparable to hydroxyl radicals, but exhibit longer lifetimes and greater selectivity toward organic contaminants [6]. However, unactivated persuphate reacts slowly with complex hydrocarbon mixtures, necessitating the use of activation strategies to enhance its oxidative efficiency [7].

Transitional metal activation, particularly using cobalt ions (Co^{2+}), has been shown to effectively catalyze persulphate decomposition into sulphate radicals through redox cycling mechanisms [6, 8]. Cobalt activated persulphate systems have demonstrated superior performance in degrading petroleum hydrocarbons, chlorinated solvents, and persistent organic pollutants [9]. Nonetheless, the efficiency of this process is strongly dependent on both persulphate dosage and catalyst concentration. Excessive cobalt concentrations may result in radical scavenging or catalyst saturation, thereby reducing oxidation efficiency and increasing secondary metal contamination risks [8]. Despite the growing body of research on persulphate based oxidation, systematic investigations on the combined effects of persulphate concentration and cobalt catalyst dosage for spent lubrication oil contaminated soils remain limited. In particular, the identification of optimal catalyst loading that maximizes degradation while minimizing radical quenching is crucial for field scale application. [5].

Therefore, this study aims to evaluate the effectiveness of persulphate oxidation at varying concentrations (1 M, 0.75 M, 0.4 M, 0.25 M, and 0.1 M) activated with different cobalt ion dosages (0.75 M, 0.25 M , and 0.1 M) for the remediation of spent lubrication oil-contaminated soil under batch microcosm conditions. The temporal degradation behavior was monitored over a 42-day

period, and treatment performance was assessed based on percentage hydrocarbon removal. The findings provide critical insights into catalyst optimization and contribute to the development of efficient sulphate radical based remediation strategies for petroleum contaminated soils.

$$S_2O_8 + [\text{Organics CHX}]_{\text{obnoxious compound}} \rightarrow CO_2 + H_2O + [\text{Inorganic residues MX}]_{\text{innocuous compound}} \quad (1)$$

Persulfate is one of the strongest oxidant that combines a high redox potential of 2.10V with a rapid nucleophilic charge-transfer capability for the half cell reaction as indicated below:

$$S_2O_8 + 2e^- \rightarrow SO_4^{2-}, E^0 = 2.10V \quad (2)$$

When persulfate is activated with a transition metal, as represented by M, one mole of persulfate will produce one mole of sulfate free radicals.

$$S_2O_8 + M \rightarrow M^+ + SO_4^{2-} + SO_4^{-}\cdot \quad (3)$$

The half-cell reaction of the sulfate free radical is

$$SO_4^{-}\cdot + e^{-}\cdot \rightarrow SO_4^{2-}, E^0 = 2.40V \quad (4)$$

This study is carried out in batches to evaluate the feasibility of persulphate to oxidize petroleum based hydrocarbon contaminated soil. Several controlling factors were evaluated, including variations in persulphate and cobalt-ion concentrations for spent oil removal, treatment duration, and comparative efficiency of persulfate on oil-contaminated soils.

The objective of this study was to evaluate the potential of persulphate as an oxidant for the enhanced degradation of spent lubrication oil in soil samples.

MATERIALS AND METHODS

Study location and sample collection

Sandy-loamy surface soil (0-10 cm depth) was collected from a football field located in Ajipowo Surulere Estate along Ondo Road, Akure, Ondo State, Nigeria. The site was considered relatively undisturbed to ensure reliable background soil conditions. Composite sampling of the soil followed standard field procedures for surface soil collection, as described in soil survey and analytical guidelines [10, 11]. Spent lubricating oil was collected from an automobile workshop in Oba-ile, Akure, Ondo State, Nigeria. The oil sample was stored in a clean, airtight container prior to use to avoid been contaminated and as well reduce evaporation [12]. Ammonium persulphate [$(NH_4)_2S_2O_8$,98.5% ; Guangdong Guanghua Sci-Tech Co.,Ltd] was used as oxidant, Cobalt (II) chloride($COCl_2.6H_2O$), 97%; Molychem, India) was applied to activate the persulphate.

Sample preparation and pre-treatment

Collected soil samples were transported to the laboratory in polythene bags. The organic materials and stones that are visible are removed manually, followed by the thorough mixing of soil samples collected from different collection spots to obtain a composite sample [13]. The soil sample was air-dried on thick cardboard for seven days at ambient temperature to reduce moisture content and stabilize the sample before treatment, in accordance with standard soil sample preparation procedures [14,15]. After air-drying, the soil was gently crushed and passed through a 2-mm sieve to obtain a uniform texture. A mechanical mixer was then used to homogenize the soil to increase surface area exposure for physicochemical interaction.

Experimental design

A sample of the prepared soil was weighed using an analytical balance. The soil was contaminated by spiking the sample with spent lubricating oil following previously documented procedures for hydrocarbon-soil interaction studies [2]. Contamination was performed at a ratio of 1 kg of soil: 100 mL of spent lubrication oil, to give 10% v/w spent lubrication oil contamination. The oil was gradually added and thoroughly mixed with the aid of a spatula and glove to ensure uniform distribution. Control (Uncontaminated) soil and oil-contaminated soil were stored in labeled containers in the chemistry laboratory for analysis. Persulphate oxidant solutions of varying molar concentrations of 1.0 M, 0.75 M, 0.40 M, 0.25 M and 0.10 M persulphate (oxidant) were prepared, along with cobalt catalyst solutions at different concentrations of 0.75 M, 0.25 M and 0.10 M for reaction activation. The persulphate and cobalt required masses where calculated based on the molar mass of persulphate (228.18 g/mol) and cobalt (129.84 g/mol). Accurately weighed amount of persulphate (228.18 g, 171.14 g, 91.27 g, 57.05 g, and 22.82 g, respectively and cobalt (178.4 g, 59.5 g, and 23.8 g, respectively) were each dissolved in distilled water and made up to a volume of 1 dm^3 in volumetric flasks. Batch experiments were conducted using 20-mL volatile organic analysis (VOA) vials, which served as reactors. Each vial was loaded with 2 g of the contaminated soil, followed by the addition of 5 mL of the oxidant solution. Subsequently, 2 mL of the catalyst solution was added to each reactor, except one vial in each batch, which contained only the soil oxidant mixture for comparative assessment. All batch experiments were conducted in duplicate and left undisturbed throughout the study to simulate the nearly static conditions characteristic of the subsurface environment.

Efficiency removal of residual oil concentration (ROC)

Residual oil in the contaminated soil was quantified using the Walkley-Black wet oxidation method for determining oxidizable organic carbon, following modifications of established procedures [16]. Briefly the vial containing the soil oxidant mixture was transferred into a 250 mL conical flask, after which 10 mL of 0.167 M potassium dichromate ($K_2Cr_2O_7$) was added. Subsequently, 20 mL of concentrated sulfuric acid (H_2SO_4) was dispensed rapidly into the flask to initiate oxidation, and the flask was swirled gently to ensure proper mixing of soil and reagents. The mixture was swirled vigorously for an additional one minute on a heat resistant asbestos sheet to enhance uniform digestion. The flask was allowed to stand for 30 min to permit oxidation, after which 100 ml of distilled water was added. Subsequently, 3-4 drops of ferroin indicator were introduced, and the mixture was titrated with 0.5 M ferrous ammonium sulfate (FAS) until the solution transitioned from dark green to a sharp brownish red (maroon) end-point. This distinct colour change signified the completion of titration. Blank titrations were performed following identical conditions but without soil to standardize the FAS solution, and mean blank values were used for calculations. All sample titrations were run in triplicate together with reagent blanks; blank volumes were used to correct sample titrations. The blank variability was maintained below 0.5 ml, ensuring analytical precision consistent with recommended methodological standards [17,18]. Method blanks and matrix spikes were included to assess interferences from residual oxidant and reaction by products from persulphate treatment. Results were reported as percent oxidizable organic carbon (OC) and converted to organic matter where required [10,19]. To reduce interference from residual oxidant generated during persulphate treatment, all soil samples were quenched prior to WB analysis by treating wet soil aliquots with excess sodium thiosulphate, confirming absence of residual oxidant by using persulfate test strip which showed no colour change before proceeding with WB titration.

$$\%\ Organic\ Carbon = \frac{(V_b - V_s)X\ M \text{ x } 0.003\ X\ f}{Weight\ of\ Soil} \text{ X } 100 \qquad (5)$$

Where V_b = volume of titrant for the reagent blank (ml)

V_s = volume of titrant for the sample (ml)

M = Molarity of Ferrous Sulphate titrant (eq.L^{-1}) [16].

0.003= grams of carbon oxidized per ml of 1.0 M dichromate equivalent (method constant)

f = correction factor for incomplete oxidation (commonly 1.30-1.33)

W= mass of oven dry soil used in analysis (g).

% Organic Matter = % Organic Carbon x 1.724

Hydrocarbon analysis using GC-MS

The spent lubrication oil extracts, both before and after six weeks of persulphate treatment, were analyzed by gas chromatography mass spectrometry (GC-MS) to identify hydrocarbon compounds and assess their relative abundances. Sample analysis was conducted on an Agilent (Hewlett-Packard) 6890 GC coupled to a 5973 mass spectrometer, using an HP-5MS fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness) [20]. The GC oven was programmed from 100 ^{0}C (1 min hold), ramped at 15 ^{0}C/min to 160 ^{0}C, then 5 ^{0}C/min to 300 ^{0}C, with a final hold of 7 min. The injector temperature was set at 280 ^{0}C, and injections were performed splitless for 3 min, with an injection volume of 0.5 μL. Helium was used as the carrier gas at 1mL/min, controlled via electronic pressure [20]. The MS transfer line (interface) was maintained at 280 ^{0}C, and the mass spectrometer operated in electron impact ionization mode (70 eV), scanning a mass range of 50-500 amu, consistent with widely used hydrocarbon profiling methods [21]. Compound identification was carried out by matching spectra against mass spectral libraries (e.g., NIST/Wiley) [21].

RESULTS AND DISCUSSION

Spent oil oxidation under different persulfate concentrations

The degradation of spent lubrication oil contaminated soil was monitored for 42 days under different persulphate cobalt catalytic conditions. All systems began with a baseline concentration of 1.00, from which reductions were calculated as percentage degradation. The control (no oxidant, no catalyst) showed minimal natural attenuation (<7%), whereas persulphate oxidation enhanced degradation significantly particularly when catalyzed by cobalt ions.

Effect of persulphate (1 M PDS) under different cobalt ion concentrations

Fig 1 illustrates the degradation behavior of spent oil under 1M persulphate treatment at varying cobalt ion concentrations. The control in the 1.0 M persulfate experiment showed that 3.41-6.82% degradation over 42 days. The low natural attenuation reflects the inherent stability of spent lubrication oil, which contains high molecular weight hydrocarbons, resins, asphaltenes, and persistent polycyclic aromatic hydrocarbons. Such compounds are well documented to degrade slowly due to low solubility and resistance to microbial enzymatic attack [22,23] Persulphate alone

achieved an initial 47.5% degradation on day 1, which gradually increased to 53.41% by day 42, indicating that unassisted persulphate oxidation can occur through natural or thermal activation within soil matrices, though its overall efficiency remains limited without catalytic enhancement [5]. In contrast, the 0.1 M cobalt-activated system showed superior catalytic performance among the low to moderate cobalt concentrations, with degradation increasing from 52.5% on day 1 to 59.09% by day 42.

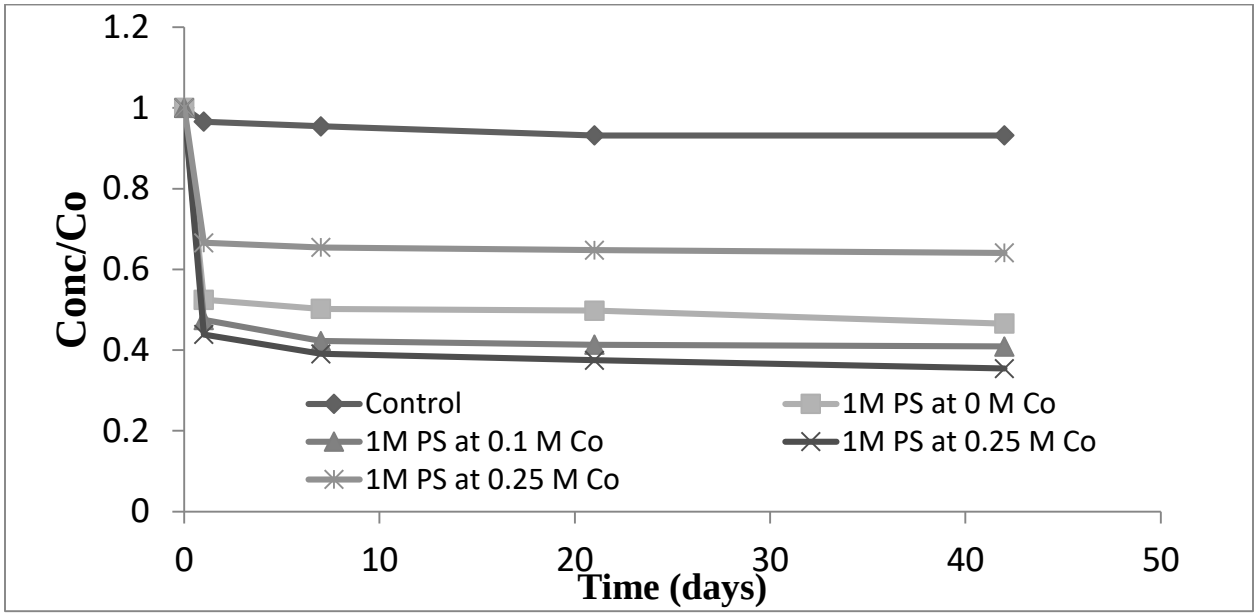

Fig. 1: Results showing 100 ml of spent oil oxidation under 1 M persulphate concentrations with different cobalt concentrations (initial spent oil concentrations: 5500 mg/kg; molar ratio of persulphate/cobalt ion: 1/ 0, 0.1, 0.25, 0.75).

This behavior is consistent with reports that optimal, moderate levels of cobalt ions enhance sulfate radical generation without promoting radical scavenging as shown in Equation 1 [24]. The 0.25 M cobalt treatment exhibited comparatively reduced degradation (33-36%), supporting evidence that excess Co^{2+} can act as a radical scavenger, thereby suppressing and diminishing oxidation efficiency [8]. In contrast, the highest cobalt dosage (0.75 M) demonstrated the greatest overall performance, with degradation increasing sharply from 56.14% on day 1 to 64.55% on day 42. This result suggests that at sufficiently high Co^{2+} concentrations, persulphate activation becomes significantly more efficient due to enhanced radical propagation, corroborating different findings

that cobalt concentrations exceeding 0.5 M can intensify sulfate radical generation [9]. The comparative trend; 0.75 M Co > 0.1 M Co > 0 M Co > 0.25 M Co > Control shows 1 M persulphate/ 0.75 M cobalt as the best performing system, achieving 64.55% degradation. While the worst performing catalytic system: 0.25 M cobalt, likely due to radical scavenging or catalyst oversaturation.

Effect of persulphate (0.75 M PDS) under different cobalt ion concentrations

The effectiveness of 0.75 M persulphate in degrading spent oil-contaminated soil varied markedly depending on the cobalt activation level. The 0.75 M persulphate control showed 4.5-6.8% degradation, confirming again that natural attenuation alone is insufficient for removing spent lubrication oil from soil. The near identical performance to the 1.0 M control indicates that the natural degradation capacity of the soil does not respond strongly to concentration differences in the untreated system. Studies have demonstrated that PAH-rich lubricating oils exhibit extremely limited biodegradability over short time scales [25, 22]. In the presence of cobalt, Fig 2 shows persulphate oxidation proceeded moderately, achieving 33.4% degradation at day 1 and reaching 43.0% by day 42. This behavior is consistent with the known characteristics of non-activated persulphate, which can undergo slow self-activation through ambient heat, soil minerals, or natural organic matter to generate sulfate radicals ($SO_4^{\cdot-}$). However, the radical yield under such conditions remains limited, resulting in only moderate hydrocarbon oxidation efficiency [5].

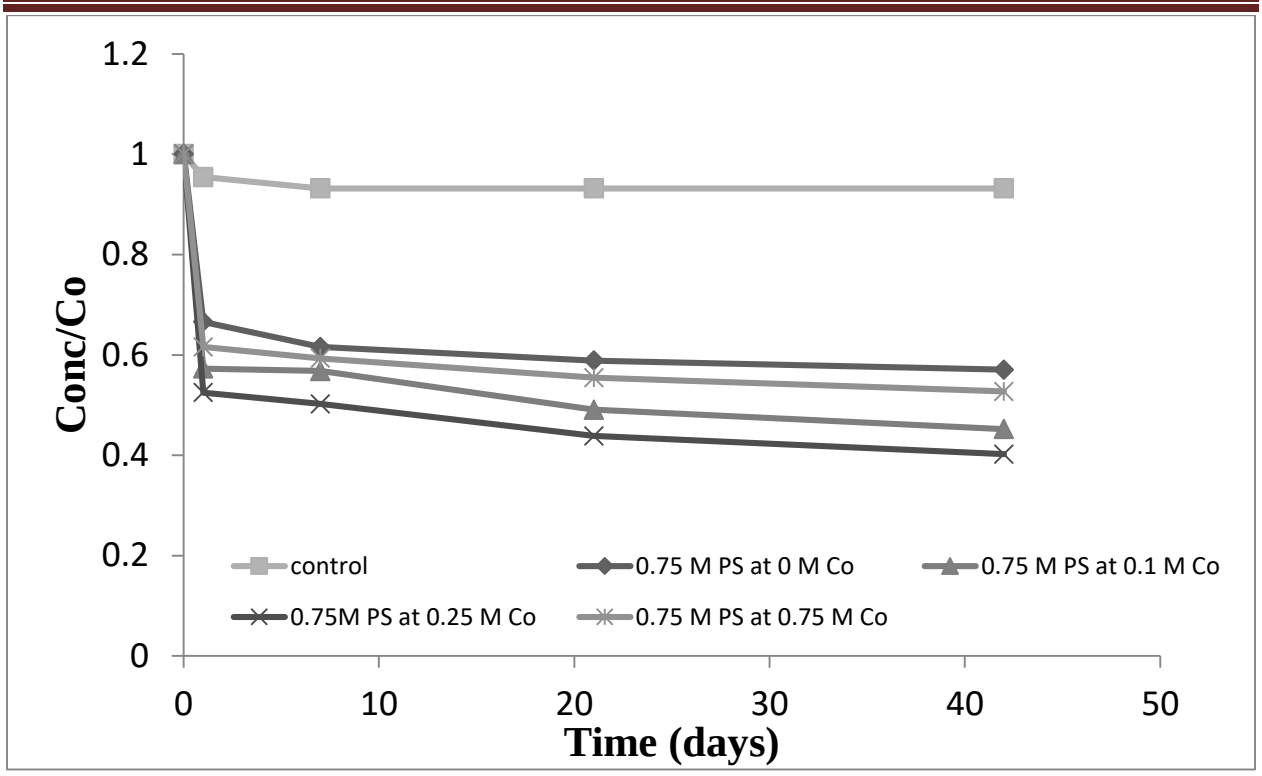

Fig. 2: Results showing 100 mls of spent oil oxidation under 0.75 M persulphate concentrations with different cobalt concentrations(initial spent oil concentrations: 5500 mg/kg; molar ratio of persulfate/cobalt ion: 1/ 0, 0.1, 0.25, 0.75).

The introduction of cobalt significantly enhanced the oxidative performance of persulphate. At 0.1 M Co^{2+}, degradation increased to 42.7% at day 1 and 54.8% by day 42, demonstrating the role of cobalt as an effective activator of persulphate. Moderate cobalt concentrations facilitate rapid persulphate decomposition and improve sulfate radical generation, thereby accelerating the breakdown of petroleum hydrocarbons without inducing radical scavenging reactions [24]. The 0.25 M cobalt ion treatment produced the highest degradation efficiencies, recording 47.5% degradation at day 1 and 59.8% by day 42, outperforming all other activation levels. This result suggests that 0.25 M cobalt provides the optimal balance between catalyst availability and radical formation. At this concentration, the system likely maximizes sulphate radical production while minimizing cobalt-induced side reactions, resulting in the most efficient oxidation of spent oil hydrocarbons. Conversely, increasing cobalt concentration beyond the optimal level resulted in diminished performance. At 0.75 M Co^{2+}, degradation decreased to 38.4% at day 1 and 47.35 at day 42, values lower than both the 0.1 M and 0.25 M cobalt treatments. This decline aligns with

established findings that excessive cobalt concentrations can act as radical scavengers, consuming sulphate radicals and thereby reducing their availability for contaminant oxidation [8]. Consequently, cobalt overdosing becomes counterproductive, suppressing rather than enhancing persulphate activation. Overall, the results show a clear catalytic threshold beyond which further increases in cobalt concentration inhibit rather than enhance oxidative degradation. The trend confirms that 0.25 M cobalt represents the optimal activation dose for 0.75 M persulphate under the conditions of this study.

Effect of persulphate (0.40 M PDS) under different cobalt ion concentrations

The 0.4 M control recorded 2.3-6.8% degradation across 42 days, the lowest of all. This supports evidence that, without stimulation, the heavier fractions in spent oil including C_{20}—C_{34} alkanes and multi-ring PAHs persist strongly in soil environments because they require oxidative activation for breakdown [26]. The minimal change across time reinforces their chemical stability. Fig 3 demonstrates persulphate alone to produce moderate degradation, achieving 32.3% removal on day 1 and stabilizing at 46.1% between days 21 and 42. This performance indicates that persulphate can oxidize hydrocarbons but at a relatively slow rate because its activation relies solely on natural soil conditions such as heat, mineral content, and organic matter. Similar observations have been reported in previous studies, where non-activated persulphate systems yielded only partial hydrocarbon oxidation [5].

When activated with cobalt, however, persulphate generates sulfate radicals ($SO_4^{\cdot}$-), which are among the most powerful oxidants used in soil remediation. The 0.1 M cobalt activated treatment produced the highest degradation efficiency across all systems, achieving 70% degradation at day 1 and 83.4% by day 42. This superior performance reflects optimal activation of persulphate at relatively low cobalt concentrations, consistent with evidence that moderate Co^{2+} levels maximize sulphate radical formation while minimizing radical quenching [24]. A strong performance was also observed with the 0.25 M cobalt treatment; however, degradation decreased to 66.6% at day 1 and 72.7% at day 42 compared to the 0.1 M Co system. This decline suggests that higher cobalt concentrations begin to scavenge sulfate radicals, thereby reducing oxidation efficiency.

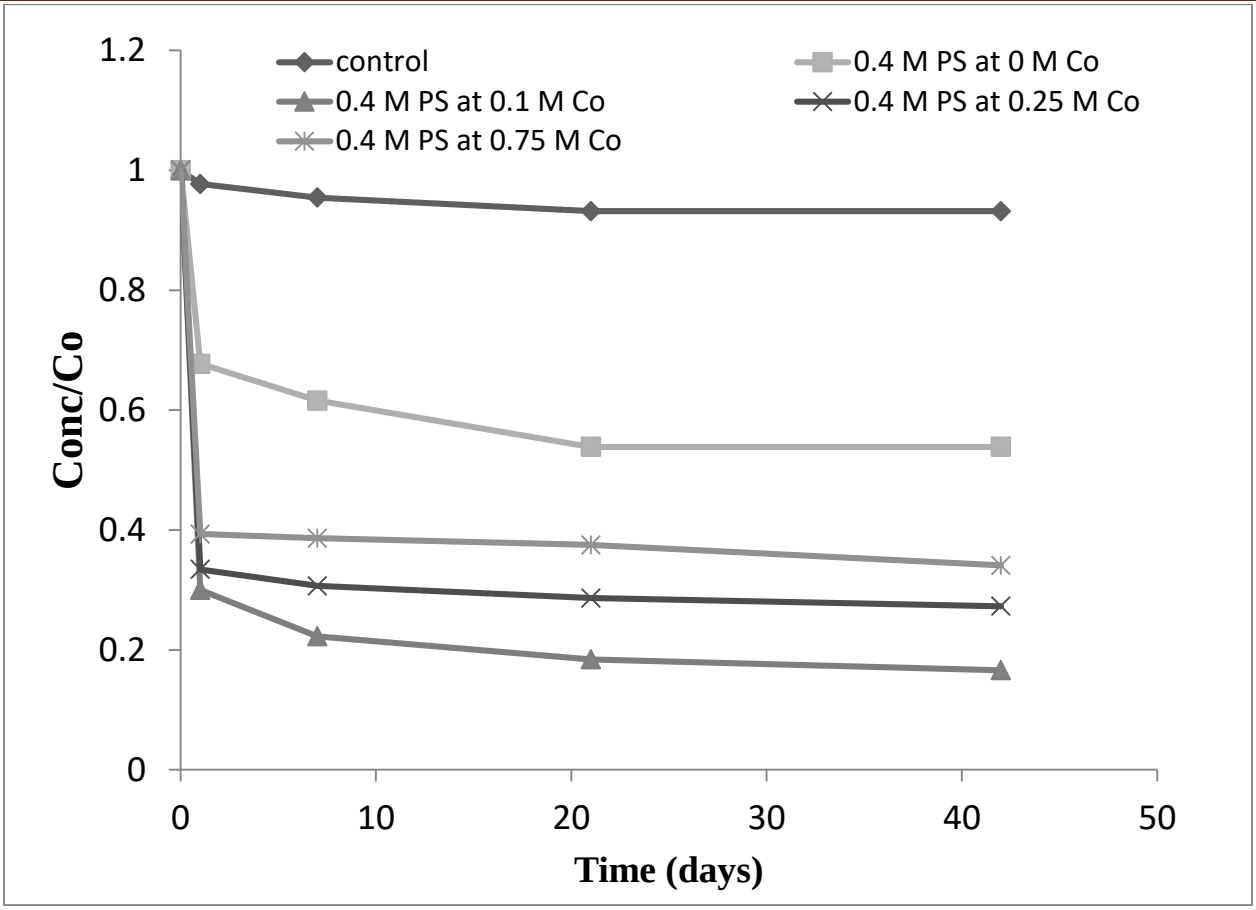

Fig. 3: Results showing 100 mL of spent oil oxidation under 0.4 M persulphate concentrations with different cobalt concentrations (initial spent oil concentrations: 5500 mgkg−1; molar ratio of persulphate/cobalt ion: 1/ 0, 0.1, 0.25, 0.75).

This trend aligns with reports showing that excess Co^{2+} diminishes $SO_4^{\cdot-}$ availability [8]. At 0.75 M cobalt, degradation rates remained higher than those of non-catalyzed persulphate but showed further decline, ranging from 60.7% at day 1 to 65.9% at day 42. This performance reduction confirms that excessively high cobalt concentrations suppress oxidation through radical scavenging, catalyst saturation, and competing side reactions. Overall, these findings indicate that while cobalt is an effective persulphate activator, its efficiency is highly concentration dependent, with overdosing leading to diminished remediation performance.

Effect of persulfate (0.25 M PDS) under different cobalt ion concentrations

The 0.25 M persulphate control also showed limited degradation (4.5—6.8%). The slight variability is consistent with previous findings showing that natural microbial communities degrade only a narrow portion of the total petroleum hydrocarbon (TPH) spectrum under non-enhanced conditions [3]. This again confirms the recalcitrance of spent lubrication oil in untreated soil. The performance of the 0.25 M persulphate (PDS) system without cobalt activation demonstrated the highest degradation efficiency among all treatments, achieving 71.6% degradation on day 1 and increasing to 88.9% by day 42 as shown in Fig 4. This strong performance indicates that, at this concentration, persulphate is sufficiently reactive to generate sulfate radicals through natural activation pathways such as soil heat, mineral surfaces and inherent organic matter. Previous studies confirm that soils containing iron and manganese bearing minerals can promote spontaneous persulfate activation, enabling substantial hydrocarbon degradation even in the absence of external catalysts [5]. Furthermore, the relatively dilute persulfate concentration limits radical-radical recombination and scavenging, thereby promoting efficient radical utilization.

Introducing 0.1 M cobalt into the 0.25 M PDS system improved activation but did not surpass the uncatalyzed treatment. Degradation reached 69.8% on day 1 and 75.4% by day 42, indicating that cobalt enhanced radical formation but also introduced competing side reactions. Given that 0.25 M persulfate already generates an optimal radical flux, the addition of cobalt likely increased radical consumption through non-productive reactions, reducing overall efficiency. This observation aligns with reports that metal-activated persulfate systems can experience reduced performance when radical generation exceeds the system capacity for effective pollutant oxidation [8].

Further increasing cobalt concentration to 0.25 M led to a noticeable decline in degradation efficiency, with 61.4% at day 1 and 72.0% by day 42. The reduction in performance indicates that excess cobalt ions can scavenge sulfate radicals, diminishing the number of radicals available for oxidizing hydrocarbons. This behavior is consistent with literature documenting the counterproductive effects of high catalyst loading, where cobalt ions quench sulfate radicals or form complexes that limit persulfate activation efficiency [8].

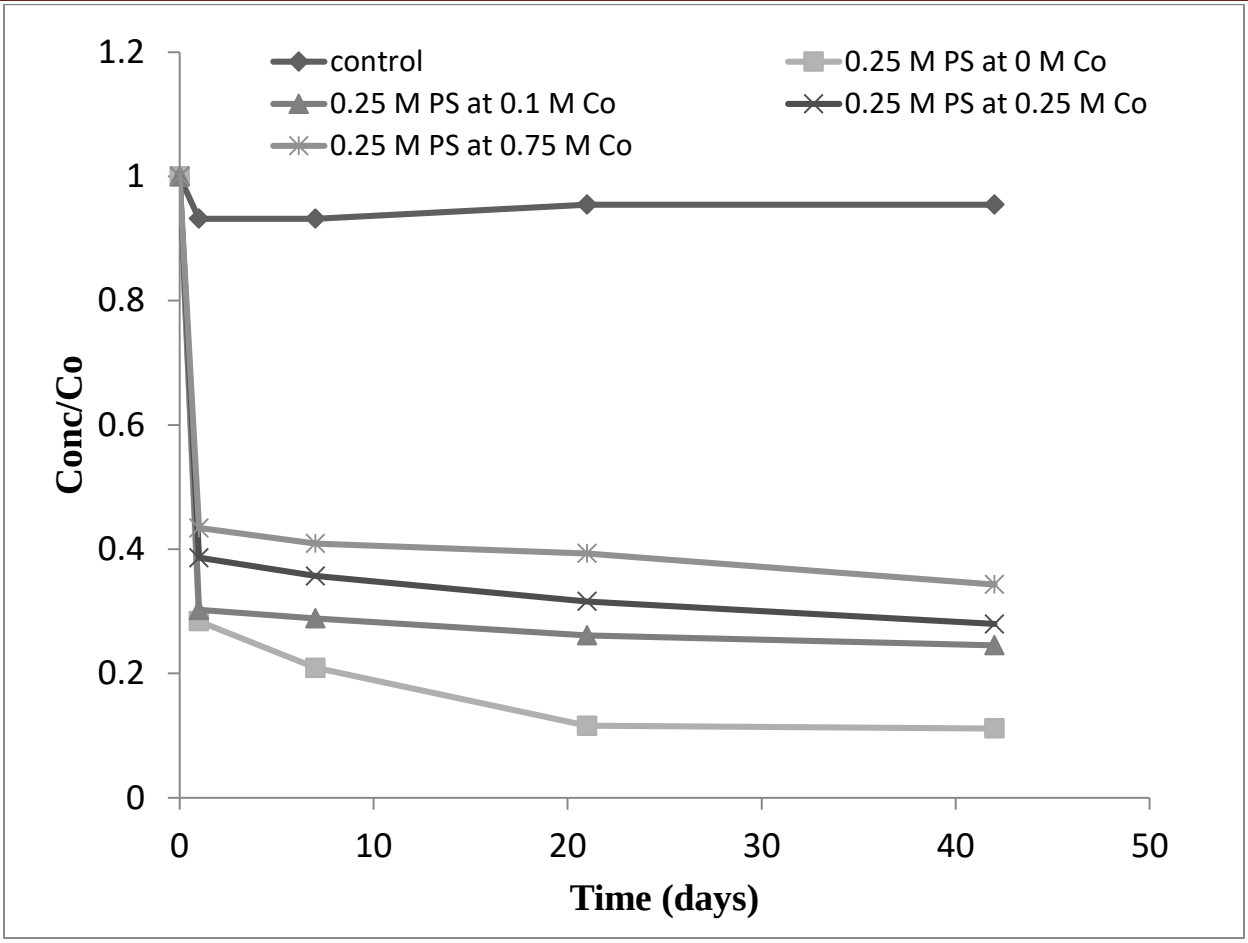

Fig. 4: Results showing 100 mL spent oil oxidation under 0.25 M persulphate concentrations with different cobalt concentrations (initial spent oil concentrations: 5500 mgkg−1; molar ratio of persulfate/cobalt ion: 1/ 0, 0.1, 0.25, 0.75).

The highest cobalt dosage, 0.75 M, produced the least effective catalytic system, recording 56.6% degradation on day 1 and 65.7% by day 42. This continued decrease in efficiency likely results from a combination of radical scavenging, formation of cobalt sulfate complexes, and potential precipitation of cobalt species under soil conditions all of which reduce the effective concentration of active radicals. High cobalt concentrations are known to inhibit persulfate oxidation pathways through radical quenching, as noted by Anipsitakis and Dionysios [24]. Overall, the performance ranking from highest to lowest after 42 days is as follows: 0.25 M PDS at 0 M Co (88.9%) > 0.25 M PDS at 0.1 M Co (75.4%) > 0.25 M PDS at 0.75 M Co (65.7%), while the control achieved less than 7% degradation. These results demonstrate that persulphate alone at the correct concentration

can outperform cobalt-activated systems, and that excessive cobalt addition becomes progressively detrimental to oxidation efficiency.

Effect of persulfate (0.1 M PDS) under different cobalt ion concentrations

The 0.1 M persulphate control exhibited the highest natural attenuation, reaching 13.6% degradation after 42 days. While still modest, this represents the optimum natural degradation performance across all control systems. However, this is still very low and insufficient for remediation standards, emphasizing the need for chemical oxidation. At 0.1 M persulfate without cobalt activation, the system achieved a relatively modest natural activation of persulfate under ambient subsurface conditions, where thermal decomposition and mineral-driven activation occur at reduced rates. Similar moderate removal efficiencies for non-activated persulfate have been widely reported, as persulfate requires either heat, UV, or catalytic metals to generate sulfate radicals effectively [24].

The introduction of 0.1 M cobalt significantly improved degradation, yielding 58% degradation on day 1 and 82.7% by day 42. This substantial enhancement demonstrates effective catalytic activation of persulphate, resulting in a higher and sustained flux of sulfate radicals.

Cobalt ions activate persulphate through an electron transfer mechanism that rapidly converts persulphate ($S_2O_8^{2-}$) into the highly reactive sulfate radical ($SO_4^{\cdot -}$), thereby accelerating hydrocarbon oxidation. This catalytic behavior is consistent with findings by Jiang *et al.* [27], who observed that cobalt is among the most efficient homogenous activators of persulphate in soil and aqueous systems. The 0.25 M cobalt treatment produced the highest degradation efficiency, achieving 72.7% removal within the first 24 h and 83.9% by day 42. The rapid initial degradation indicates intense radical production and enhanced reaction kinetics.

The slight improvement over 0.1 M cobalt system suggests that 0.25 M represents an optimal catalytic balance sufficient to maximize radical generation without triggering significant radical cation side reactions. This trend aligns with studies showing that catalytic dosage strongly governs the yield and stability of sulfate radicals in metal-activated systems [28].

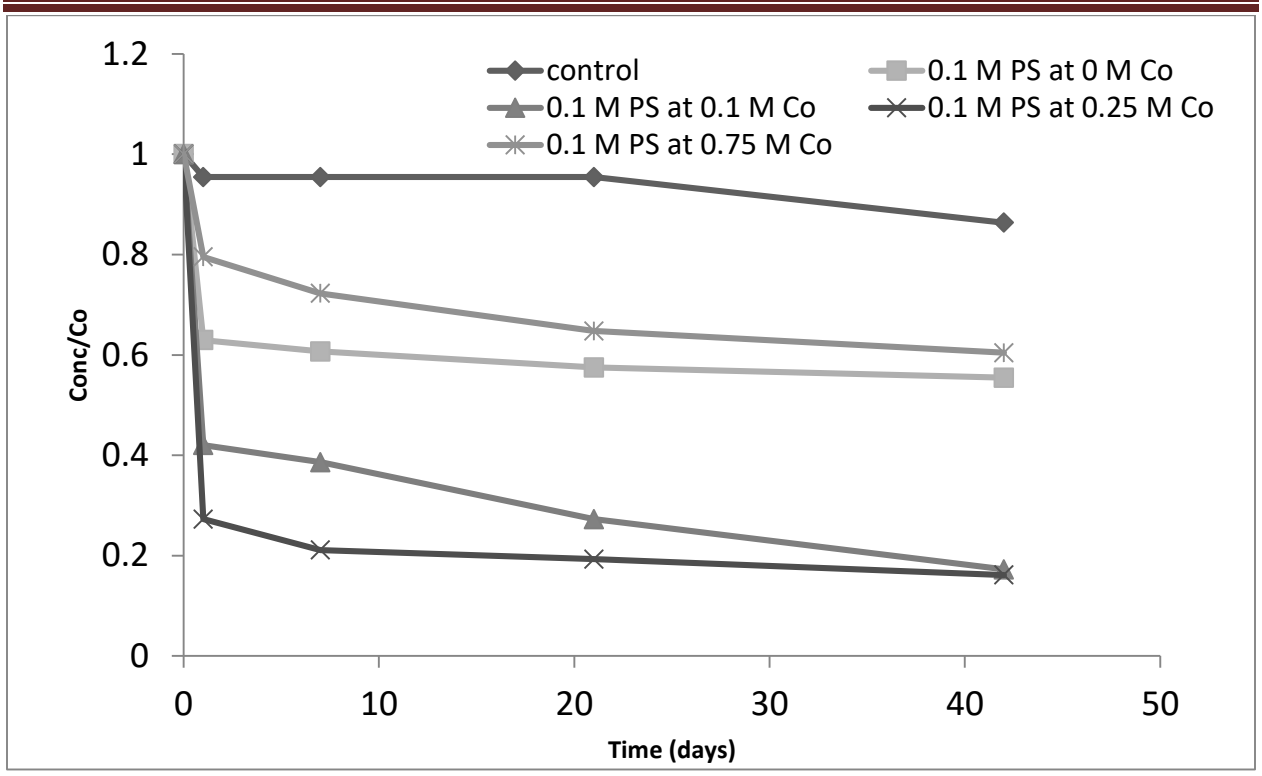

Fig. 5: Results showing 100 mL of spent oil oxidation under 0.1M persulfate concentrations with different cobalt concentrations (initial spent oil concentrations: 5500 mgkg^{-1}; molar ratio of persulfate/cobalt ion: 1/ 0, 0.1, 0.25, 0.75).

However, when cobalt concentration increased to 0.75 M, degradation efficiency declined markedly, reaching only 39.5% at day 42. This reduction is attributed to cobalt overdosing, which can cause (i) radical scavenging by excess Co^{2+} ions, (ii) precipitation or complex of cobalt species that reduce catalytic activity, and (iii) decreased availability of active sulfate radicals. Such inhibitory effects at high metal concentrations have been documented in persulphate activation systems, where catalyst overdosing leads to diminished oxidant efficiency [28]. Collectively, the results indicate that 0.1 M PDS + 0.25 M Co provides the optimal activation conditions, yielding the highest degradation rate and demonstrating the most efficient radical production. These findings underscore the importance of balancing oxidant and catalyst concentrations to achieve effective remediation without inducing radical quenching or catalyst inhibition.

CONCLUSION

The effectiveness of persulphate oxidation, with and without cobalt activation, for the remediation of spent lubrication oil contaminated soil was assessed. The results revealed that natural attenuation was insufficient, yielding minimal degradation over the experimental period, thereby confirming the recalcitrant nature of spent lubrication oil in soil matrices. Persulphate-based treatments significantly enhanced hydrocarbon degradation, with performance strongly influenced by both persulphate concentration and cobalt dosage.

Across all persulphate levels investigated, cobalt activation markedly accelerated degradation by promoting the generation of sulphate radicals, leading to rapid and substantial contaminant removal. However, the catalytic effect of cobalt was highly dose dependent. Moderate cobalt concentrations consistently produced superior degradation efficiencies, whereas excessive cobalt loading resulted in diminished performance, likely due to sulphate radical scavenging and reduced oxidant utilization. This trend was evident particularly at lower persulphate concentrations, where optimal cobalt dosing achieved degradation efficiencies exceeding 80%, while higher cobalt concentrations led to noticeable declines in treatment efficiency. Overall, the findings highlight that effective remediation using persulphate oxidation requires careful optimization of both oxidant and catalyst concentrations.

This study confirmed that cobalt activated persulphate is a robust and efficient chemical oxidation strategy for treating spent lubrication oil contaminated soils, provided that catalyst overdosing is avoided. These results contribute valuable insight for the design of persulphate based in situ chemical oxidation systems and support their practical application in the remediation of petroleum hydrocarbon impacted environments.

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