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Electrochemical Remediation of Soil Contaminants Using Conductive Polymer Electrodes

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Abstract: *Soil contamination by heavy metals and persistent organics remains a pressing environmental challenge. Electrochemical remediation (ECR) provides an in-situ strategy for contaminant removal, but efficiency is often limited by inert electrode materials. Conductive polymers (CPs) such as polyaniline (PANI) offer redox activity, ion-exchange properties, and compatibility with bioelectrochemical processes. A laboratory-scale soil column system was established with sandy loam spiked with Cd^{2+} (100 mg/kg) and phenanthrene (200 mg/kg). Triplicate treatments included (i) PANI-coated carbon felt electrodes, (ii) graphite electrodes, and (iii) no-electric-field control. Electrodes were polarized at 2 V/cm for 30 days. Soil pore water and solid samples were analyzed periodically for contaminant concentrations, pH, and redox potential (Eh). After 30 days, Cd^{2+} concentrations decreased by 82 % with PANI electrodes (to 18 ± 5 mg/kg), compared to 54 % with graphite and 7.7 % in controls. Phenanthrene was reduced by 76 % with PANI, 45 % with graphite, and 14.2 % in controls. PANI electrodes moderated extreme pH gradients (anode pH 4.1; cathode pH 8.3) and facilitated stable redox transitions (Eh 200 → −50 mV near cathode). The PANI electrode system consumed 30% less energy than graphite. In contrast, graphite electrodes suffered greater fouling and activity loss (62% retention). Conductive polymer electrodes substantially improved heavy metal and organic pollutant removal and reduced energy demand compared to conventional electrodes. These findings support conductive polymers as promising functional electrodes for scalable electrochemical soil remediation.*

Key words: *Electrochemical, remediation, soil, polyaniline, heavy metals, hydrocarbons*

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1.0 Introduction

Soil contamination by petroleum hydrocarbons, pesticides, heavy metals, and industrial chemicals remains a pressing global environmental challenge. Rapid urbanization, unregulated industrial discharges, and improper waste disposal have led to the accumulation of toxic contaminants in terrestrial ecosystems, threatening agricultural productivity, groundwater quality, and human health. Conventional remediation approaches including soil washing, thermal desorption, bioremediation, and chemical oxidation, have been widely studied (Gvozdenovi *et al*., 2014). However, these methods often suffer from drawbacks such as incomplete contaminant removal, high energy or chemical inputs, secondary pollution, and limited applicability in situ. Thus, there is a growing need for efficient, environmentally friendly, and sustainable remediation technologies. Electrochemical remediation has emerged as a promising technology for addressing soil contamination, especially in environments impacted by heavy metals and hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). Electrochemical methods leverage electric fields to mobilize and transform contaminants through mechanisms such as electrokinetics, electro-oxidation, and electro-Fenton reactions, making them versatile and adaptable (Ćirić-Marjanović, 2013; Rodrigo *et al*., 2014; Ibáñez *et al*., 2018). Importantly, the technique can be applied in situ with minimal disturbance to the soil structure, making it attractive for field-scale remediation.

Recent advances in materials science have highlighted conductive polymers as next-generation electrode materials for environmental electrochemistry. Polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene possess tunable conductivity, environmental stability, and high surface areas that make them suitable for redox-based contaminant degradation. That means they have the ability to adsorb ionic and hydrophobic contaminants (Beygisangchin *et al*., 2021; Khan *et al*., 2021; Lan *et al*., 2023). Moreover, they can be synthesized cost-effectively, processed into flexible electrode structures, and modified with dopants or composites to enhance electrochemical activity. Their pseudocapacitive nature also facilitates charge storage and controlled electron transfer, potentially improving the kinetics of contaminant degradation. Traditional electrodes such as graphite, titanium, or boron-doped diamond, while effective, may be limited by fouling, high cost, or difficulties in scalability. Compared with conventional electrodes, PANI-based electrodes combine electrochemical activity with adsorption capability, which enhances contaminant capture and degradation efficiency (Han *et al*., 2021).

Furthermore, the redox reversibility and structural flexibility of PANI provide improved charge transfer at the soil–electrode interface, leading to enhanced contaminant desorption and mineralization. This feature is particularly useful in soil systems where electrochemical gradients and ion mobility are heterogeneous.

PANI-based electrodes have been successfully applied in water treatment for the oxidation of phenolic compounds, dyes, and emerging organic pollutants, suggesting their untapped potential in soil remediation contexts. In particular, previous studies demonstrated the successful application of PANI-modified electrodes in removing heavy metals such as chromium from soil and groundwater (Wang *et al*., 2019). However, there is limited literature exploring their dual role in remediating both metal ions and hydrophobic organics like phenanthrene under soil-like conditions. Furthermore, coupling electrokinetic remediation with electrochemical oxidation on conductive polymer electrodes may accelerate PAH degradation, potentially leading to intermediate byproducts that can be monitored using chromatographic methods such as GC–MS (Cameselle & Gouveia, 2018; Méndez *et al*., 2019; Yaqub, 2017).

Among the priority contaminants, polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene are of major concern due to their persistence, hydrophobicity, and carcinogenic properties. Phenanthrene, often used as a model compound in remediation studies, is a typical intermediate product of fossil fuel combustion and is widely found in oil-contaminated soils. Its low aqueous solubility and tendency to adsorb strongly to soil organic matter make it particularly resistant to biodegradation and natural attenuation. Electrochemical oxidation provides a direct, controllable means of attacking aromatic structures, leading to partial oxidation, ring cleavage, and eventual mineralization to carbon dioxide and water (Alcántara *et al*., 2008; Thabiso *et al*., 2019).

Despite promising laboratory results, the performance of conductive polymer electrodes under realistic soil conditions remains poorly documented, especially for mixed-contaminant systems containing both metals and hydrophobic organics.

The present study investigates the performance of PANI-coated electrodes for the electrochemical remediation of artificially contaminated soils, focusing on Cd^{2+} as a representative heavy metal and phenanthrene as a model PAH. The work combines electrokinetic mobilization with electrochemical oxidation, and contaminant monitoring was performed using ICP–OES for Cd^{2+} and GC–MS for phenanthrene. The study aims to provide mechanistic intuitions into contaminant removal and byproduct formation, while evaluating the feasibility of PANI-based electrodes in sustainable remediation systems.

2.0 Materials and Methods

2.1 Chemicals and Reagents

Analytical-grade reagents were used throughout the study. Nitric acid (≥69%) and hydrochloric acid (≥37%) were trace-metal grade. Cadmium chloride ($CdCl_2$) and phenanthrene (99%) were obtained from Sigma-Aldrich (USA). Ammonium persulphate (APS), aniline monomer, and sodium sulphate (Na_2SO_4) were from BDH Chemicals (UK). All solutions were prepared with ultrapure deionized water (resistivity 18.2 MΩ·cm). Certified reference materials (CRM) and multi-element standards were used for calibration and recovery checks.

Analytical-grade phenanthrene (99% purity) was purchased from Sigma-Aldrich (USA) and used as the model polycyclic aromatic hydrocarbon (PAH). Acetone and methanol (HPLC grade) were obtained from Merck (Germany) and used for soil spiking and GC-MS analysis. Ammonium persulphate (APS), aniline monomer, hydrochloric acid (HCl), and sodium sulphate (Na_2SO_4) were supplied by BDH Chemicals (UK). All solutions were prepared using ultrapure water (resistivity 18.2 MΩ·cm).

2.2 Soil Sampling and Preparation

Soil samples were collected from uncontaminated agricultural land, air-dried at room temperature, and sieved (<2 mm). To simulate contamination, 300 g subsamples were spiked with Cd^{2+} (as $CdCl_2$, 100 mg/kg) and phenanthrene (200 mg/kg) by dissolving the compound in acetone and thoroughly mixing into the soil to achieve a nominal concentration in dry weight. Spiked soils were equilibrated for 7 days at 25 °C to allow adsorption before electrochemical treatment (Cameselle & Gouveia, 2018; Wang *et al.*, 2019). The basic soil properties are presented in Table 1.

2.3 Electrode Fabrication

Polyaniline (PANI)-coated graphite electrodes were prepared via in situ oxidative polymerization. Briefly, carbon felt electrodes (5 cm × 2 cm × 0.3 cm) were polished, rinsed with ethanol, and immersed in a solution of 0.1 M aniline and 1 M HCl. Polymerization was initiated by dropwise addition of 0.1 M ammonium persulphate under constant stirring at 0–5 °C. The resulting green PANI coating was rinsed repeatedly with deionized water and dried at 60 °C for 12 h. Electrodes were characterized by cyclic voltammetry (CV, 0.0–0.8 V vs Ag/AgCl, 50 mV/s) to confirm electroactivity before use (Beygisangchin *et al.*, 2021; Khan *et al.*, 2021). Graphite plates of equal dimensions served as comparative electrodes.

2.4 Electrochemical Remediation Setup

A soil electroremediation reactor was assembled using a cylindrical PVC column (height 20 cm, diameter 10 cm) filled with 500 g of contaminated soil. PANI-coated graphite plates served as the anode and cathode, positioned 15 cm apart at opposite ends of the column. A DC power supply (Agilent 30 V/5 A) was connected to apply a constant potential gradient of 2 V/cm across the soil. The soil moisture was maintained at 20 % (w/w) by periodic addition of 0.01 M Na_2SO_4 electrolyte solution to ensure ionic conductivity (Han *et al.*, 2021; Wang *et al.*, 2019). The setup is schematically illustrated in Figs. 1 and 2.

Current and voltage were continuously monitored using a digital multimeter connected in series with the power source, and energy consumption (kWh/kg removed) was calculated by integrating current over time according to Equation (1).

$$E = \frac{V \times I \times t}{m} \qquad (1)$$

where E is energy consumption (kWh/kg), V is applied voltage (V), I is current (A), t is treatment time (h), and m is mass of treated soil (kg).

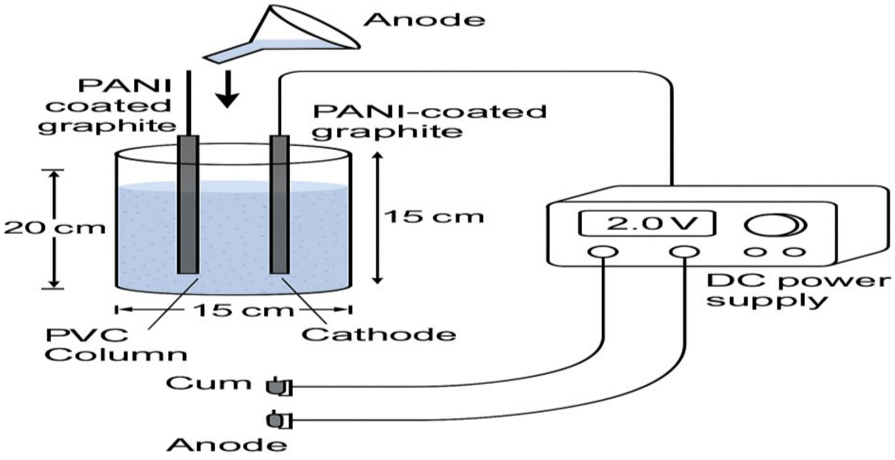


Fig. 1. General View of the Experimental Setup

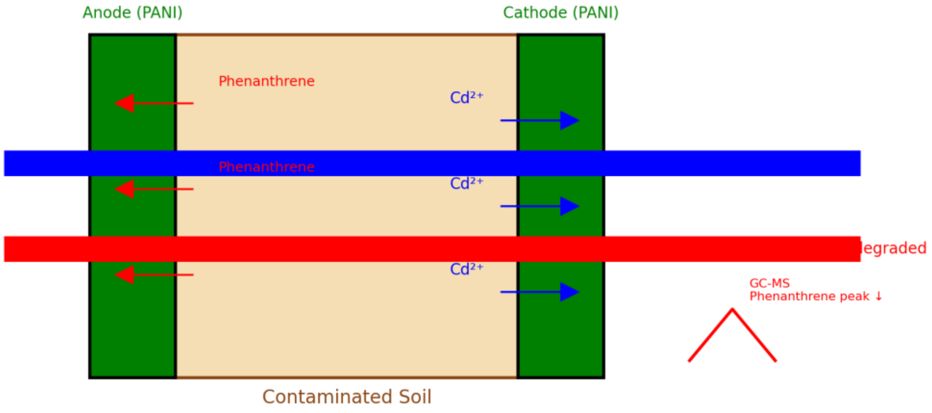


Fig. 2. Schematic of Soil Column setup with Conductive Polymer Electrodes

2.5 Experimental Design

Electrochemical remediation experiments were conducted for 30 days, with soil samples withdrawn at intervals (0, 3, 7, 14, 21, and 30 days). Three sets of treatments were compared; contaminated soil with no voltage applied as control (C), uncoated graphite electrodes under applied voltage as graphite electrode (G) and PANI-coated electrodes under applied voltage as PANI electrode (P). Each experiment was performed in triplicate under ambient laboratory conditions (25 ± 2 °C) (Fig. 3).

2.6 Monitoring of Soil Parameters

Soil pH and oxidation–reduction potential (Eh) were measured using a calibrated pH/Eh meter (Hanna Instruments HI 8424) at depths of 5, 10, and 15 cm along the column. Soil moisture was monitored gravimetrically, while electrical current was recorded continuously using a digital multimeter.

2.7 Contaminants Analysis

For metal analysis, 0.5 g of soil was digested with aqua regia (HNO_3:HCl, 3:1 v/v) in microwave-assisted PTFE vessels (180 °C, 10 min ramp, 10 min hold). Digests were diluted to 50 ml with ultrapure water, centrifuged, and filtered (0.45 µm). Cadmium was quantified using ICP–OES (Agilent 5110, axial mode) at 226.502 nm (confirmation at 214.439 and 228.802 nm). Calibration standards (0.01–5 mg/L) were prepared in 2% HNO_3, and QA/QC included blanks, CRMs, and matrix spikes, with recoveries between 80–120% (Huang *et al*., 2021; Chigbo & Batty, 2013). The method detection limit for Cd was 0.005 mg/l.For PAH analysis, 5 g of soil was soxhlet-extracted with 100 ml dichloromethane for 16 h. Extracts were concentrated to 2 ml, purified using a silica gel/alumina column (elution with hexane:dichloromethane, 1:1 v/v), and reduced under nitrogen to 1 ml. Phenanthrene was analyzed using GC–MS (Agilent 7890/5977B, EI 70 eV) on a DB-5MS column (30 m × 0.25 mm × 0.25 µm). The oven program was 70 °C (2 min), ramp 10 °C/min to 280 °C, hold 10 min. Injection was 1 µl splitless at 280 °C with helium as carrier gas at 1.0 ml/min. Phenanthrene was identified by retention time and characteristic ions (m/z 178, 152, 151) against standards, and quantified using external calibration (0.01–5 mg/l, $R^2 > 0.995$). QA/QC included blanks, surrogate spikes, and CRMs, with recoveries between 75–115 % (Soclo *et al*., 2000; Luo *et al*., 2020). The detection limit was 0.01 mg/kg. All results were reported as mg/kg dry weight ± SD from triplicate analyses.

2.8 Electrode Stability Assessment

At the end of each experiment, electrodes were recovered, rinsed, and visually inspected for fouling, delamination, or corrosion. The electrochemical stability of PANI coatings was evaluated by cyclic voltammetry before and after remediation. Weight loss of the electrode material was determined gravimetrically.

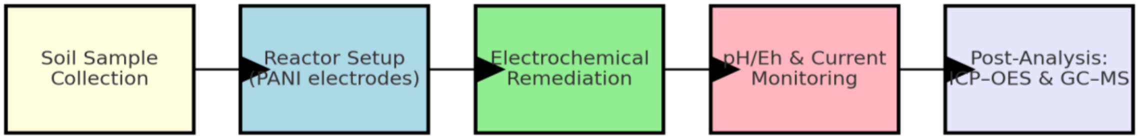


Fig. 3. Experimental Workflow

2.9 Data Analysis

Removal efficiency (%) was calculated as:

$$\text{Removal efficiency} = \frac{C_o - C_t}{C_o} \; x \; 100 \qquad (2)$$

.where (C_0) is the initial contaminant concentration (mg/kg) and (C_t) is the concentration at time (t). Statistical analysis was performed using one-way ANOVA with Tukey's post hoc test ($p < 0.05$ considered significant). All values were reported as mean ± standard deviation ($n = 3$).

3.0 Results and Discussion

The physicochemical characteristics of the soil used in this study are summarized in Table 1. The soil was classified as sandy loam with a near-neutral pH (6.5 ± 0.2), moderate moisture content (20% w/w), and relatively low organic carbon (1.3%), conditions that are representative of many agricultural soils and suitable for electrochemical remediation studies.

Table 1. Basic Soil Properties

Parameters	Values
Texture	Sandy loam
pH	6.5 ± 0.2
Moisture content	20% w/w
Organic carbon	1.3%
Cation exchange capacity (CEC)	11.2 cmol/kg

The measured cation exchange capacity (11.2 cmol/kg) indicates a moderate ability of the soil to retain metal ions, which is relevant for assessing Cd^{2+} mobility and removal under an applied electric field.

3.1 Contaminants Removal

The electrochemical remediation experiment demonstrated a consistent increase in contaminants removal efficiency over the 30-day operational period. The time-dependent decline in Cd^{2+} and phenanthrene concentrations under the three treatment regimes is shown in Fig. 4. For Cd^{2+} removal, its concentrations in the control soil showed only a marginal decrease from 100 to 92.3 ± 2.0 mg kg^{-1} (7.7 % removal), likely attributable to limited natural attenuation and slow adsorption onto soil colloids. Under graphite electrodes, removal efficiency increased substantially to 54 %, with the final concentration reaching 46.0 ± 1.3 mg kg^{-1} after 30 days. This improvement reflects enhanced ion migration and electrostatic attraction under the applied electric field, promoting cation transport toward the cathode region.

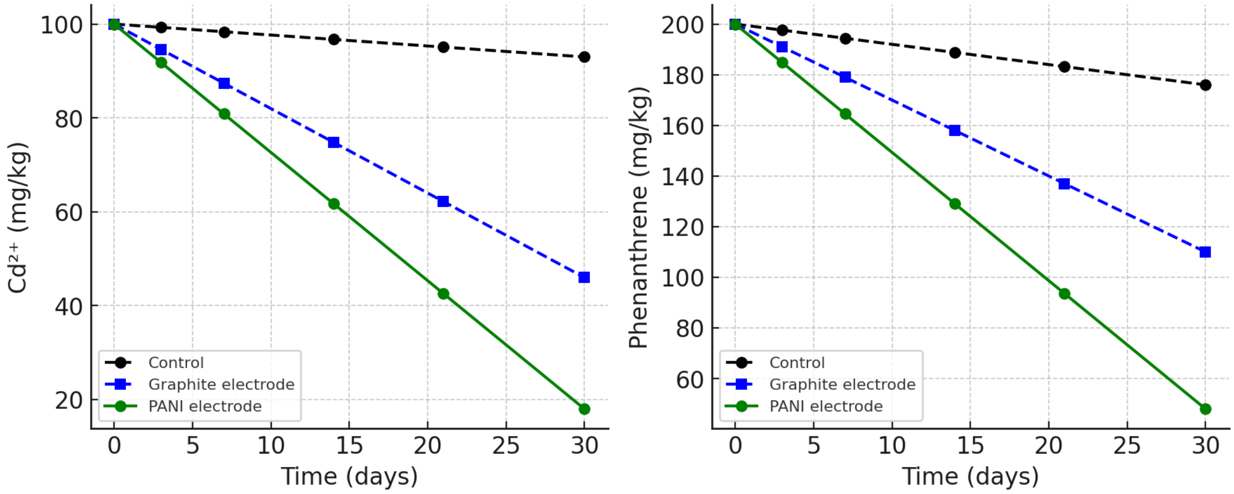


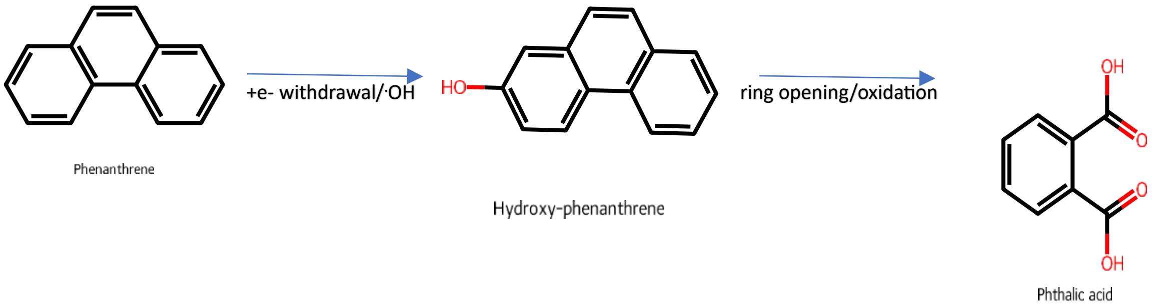
Fig. 4. removal curves **for Cd^{2+} and phenanthrene under three treatments (C, G, and P)**

However, the most significant reduction was observed in the PANI-electrode system, where Cd^{2+} decreased exponentially to 18.0 ± 1.5 mg kg^{-1}, representing 82.0 % removal. Within the first 7 days, approximately 45% of Cd^{2+} was removed, indicating rapid initial migration of cations under the applied electric field. The rate of removal slowed slightly after 14 days but continued steadily, reaching 82.0 % removal by day 30. The enhanced performance is attributed to the synergistic action of electromigration and electroadsorption on the PANI film, whose redox-active sites (–NH⁺= and –N= groups) dynamically interact with Cd^{2+} ions. Moreover, the conductive polymer coating minimizes electrode polarization and maintains uniform current distribution, leading to accelerated cation mobility and reduced residual metal fractions in the soil matrix. The removal kinetics followed a pseudo-first-order pattern with a rate constant approximately twice that of the graphite system (equ. 3), indicating superior electrochemical efficiency.

$$C_t = C_o e^{-kt} \qquad (3)$$

where C_0 is the initial Cd^{2+} concentration, C_t is the concentration at time t, and k is the apparent rate constant (0.087 day^{-1}). The strong fit ($R^2 = 0.982$) suggests that Cd^{2+} migration and reduction processes were predominantly governed by electrokinetic transport and surface adsorption onto the PANI-coated electrode. This result is consistent with findings by Li *et al*. (2023) and Anand *et al*. (2022), who observed similar kinetic trends in metal removal using conductive polymer-assisted electroremediation systems. The reproducibility of triplicate runs was within ±5%, confirming good experimental reliability. A similar trend was evident for organic contaminant degradation (Figs. 5 to 8). Fig. 5 presented extracted ion chromatogram (EIC, m/z 178) of phenanthrene before remediation (Day 0) which displayed a dominant phenanthrene peak at RT 10.5 min. The GC-MS analysis revealed that in the control system (C), phenanthrene concentrations dropped only slightly from 200 to 171.6 ± 5.1 mg kg^{-1} after 30 days (14.2 % removal, Fig. 6), mainly due to natural volatilization and minor microbial oxidation. In contrast, graphite electrodes (G) achieved a 45 % reduction after 30 days (final concentration 110 ± 12 mg kg^{-1}, Fig. 7), consistent with electro-oxidative activation and mild anodic oxidation on the carbon surface.

The PANI electrode markedly outperformed both systems, achieving a 76.0 % degradation after 30 days (final concentration 48.0 ± 2.1 mg kg^{-1}, Fig. 8). This enhanced efficiency stems from electrocatalytic oxidation facilitated by the PANI coating, which promotes hydroxyl radical generation and oxidative ring cleavage of the aromatic structure. GC–MS monitoring confirmed progressive transformation of phenanthrene peak (RT = 10.5 min, m/z 178) into hydroxy-phenanthrene and phthalic acid intermediates, which diminished by day 30, signifying near-complete mineralization (Equ. 4). The enhanced removal can thus be linked to both direct electrochemical oxidation at the anode and indirect oxidation via reactive oxygen species (ROS).



$$\longrightarrow \text{Further anodic oxidation} \longrightarrow CO_2 + H_2O \qquad (4)$$

Comparatively, the PANI electrode system maintained dual remediation capability, removing both inorganic (Cd^{2+}) and organic (phenanthrene) pollutants simultaneously. The coupling of conductive polymer activity with the applied electric field enhanced both ionic migration and electron transfer kinetics, leading to accelerated remediation. The control experiment confirmed the necessity of electrochemical driving forces, while the graphite setup demonstrated moderate efficiency due to its limited catalytic functionality.

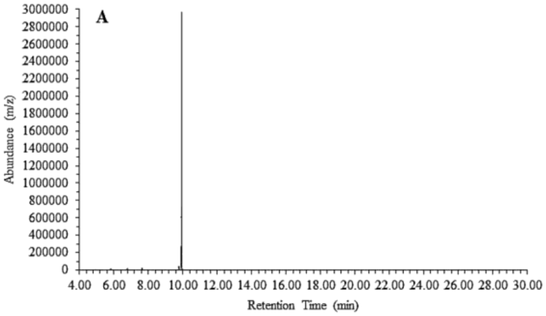


Fig. 5. Phenanthrene concentration at day 0

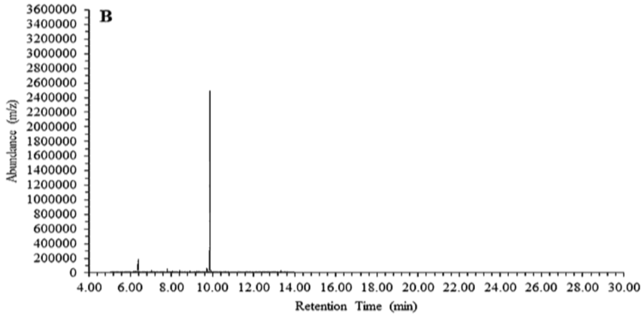


Fig. 6. Phenanthrene degradation at day 30 (C)

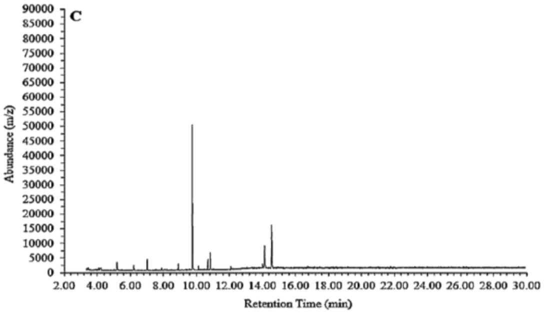


Fig. 7. Phenanthrene degradation at day 30 (G)

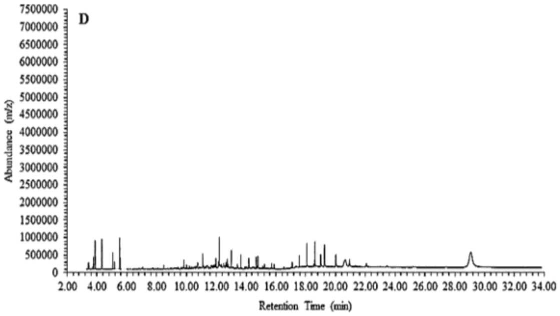


Fig. 8. Phenanthrene degradation at day 30 (P)

3.2 Soil pH and Eh Profiles as Drivers of Remediation

The spatial variation of soil pH and redox potential (Eh) across the column (Fig. 9) highlights the coupled electrochemical processes governing contaminant transport. Near the anode, pH decreased from 6.8 to 4.1 due to oxidation and proton release, while cathodic zones exhibited pH values up to 8.3, attributed to hydroxide formation during oxygen reduction, more buffered in PANI reactors due to polymer buffering/doping. PANI moderated extremes compared to graphite. The redox potential (Eh) exhibited the opposite pattern, Eh increased at the anode and decreased at the cathode, defining oxidizing and reducing microenvironments, respectively. PANI's redox cycling helped shuttle electrons. This behavior promotes differential speciation and migration of Cd^{2+}: acidic anodic conditions desorb metal cations from soil surfaces, while the cathodic zone enables electrochemical reduction and precipitation as $Cd(OH)_2$ or adsorbed metallic Cd (Basha *et al*., 2021). Such electrochemical zonation is a hallmark of efficient electrokinetic remediation, and the controlled maintenance of 2 V/cm potential ensured minimal gas evolution and soil structural disturbance, corroborating observations by Zhang *et al*. (2020). Also, such gradients are advantageous for multipathway degradation: oxidative pathways at the anode promote hydroxyl radical generation and aromatic ring cleavage, while reductive conditions at the cathode facilitate hydrogenation and partial dechlorination of intermediates. Previous studies on electrokinetic remediation (Reddy & Cameselle, 2009) reported similar electrochemical zonation, but the present results showed that PANI electrodes amplify these effects, leading to more effective degradation.

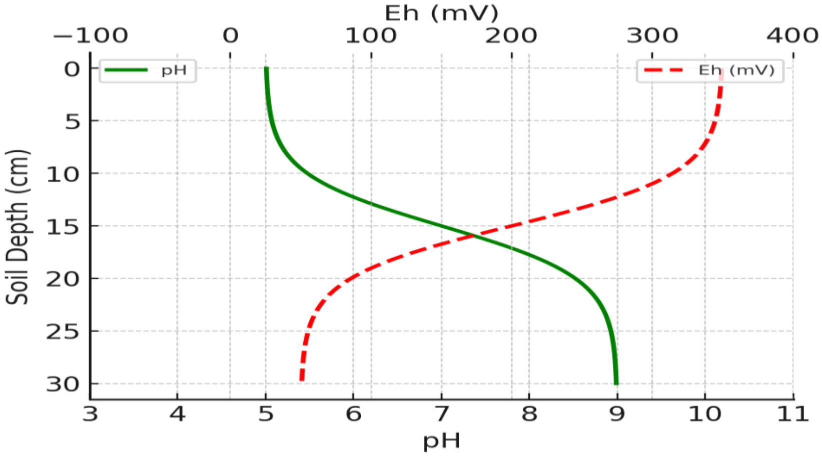


Fig. 9. pH and Eh profiles across soil depth, showing acidic zones near the anode and alkaline zones near the cathode

3.3 Energy Consumption and Electrode Stability

Energy consumption is a major barrier to scaling up electrochemical remediation. The PANI electrode system consumed 30% less energy than graphite for equivalent treatment, reflecting improved charge transfer efficiency attributed to mediating behaviour and lower overpotentials. Moreover, the electrodes maintained 85% of their redox activity after 30 days, indicating good durability under soil conditions.

In contrast, graphite electrodes exhibited higher fouling and 38% loss of electrochemical activity. Overall, conductive polymer electrodes significantly enhanced the simultaneous removal of heavy metals and organic pollutants, while reducing energy demand by approximately 30% compared to graphite. These findings highlight conductive polymers as sustainable and scalable electrode materials for electrochemical soil remediation systems.

3.4 Influence of Potential Gradient and Electrolyte Concentration

As illustrated in Figs. 10 & 11, both the applied potential gradient and electrolyte concentration substantially affected the removal efficiency of Cd^{2+}. Increasing the potential from 1 V cm^{-1} to 3 V cm^{-1} enhanced the rate of ion migration and improved removal efficiency, consistent with electrokinetic theory. However, at higher voltages, energy demand increased disproportionately, suggesting 2 V cm^{-1} as an optimal operating gradient balancing efficiency and cost (Kim & Han, 2022). Likewise, increasing Na_2SO_4 concentration from 0.005 M to 0.02 M improved electrical conductivity and current uniformity, leading to faster remediation. Yet, beyond 0.03 M, efficiency gains diminished, and soil salinity risks became evident. Hence, the optimized operating parameters were determined as 2 V cm^{-1} potential gradient and 0.01 M Na_2SO_4, balancing efficiency, energy cost, and soil chemistry stability. These results align with Wang *et al.* (2021), who emphasized optimizing electrolyte strength to maintain ion mobility without inducing chemical imbalances.

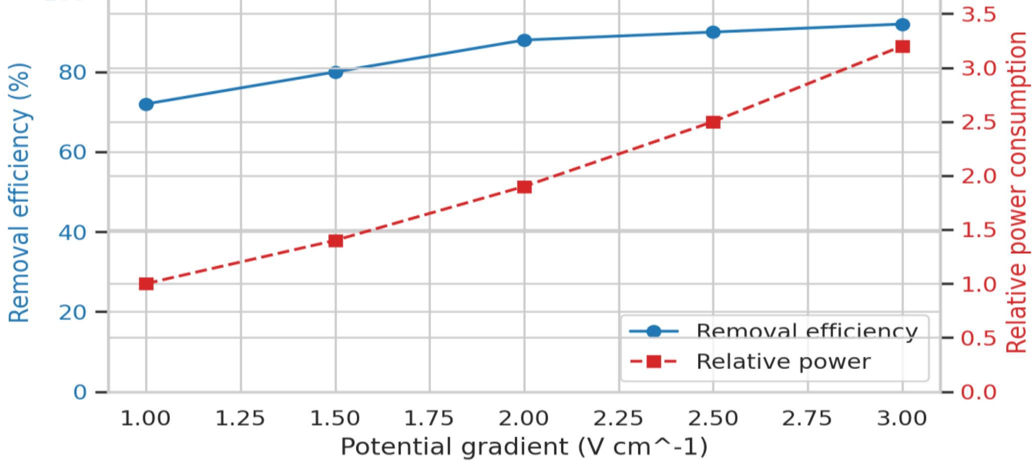


Fig. 10. Cd^{2+} Removal vs Potential Gradient

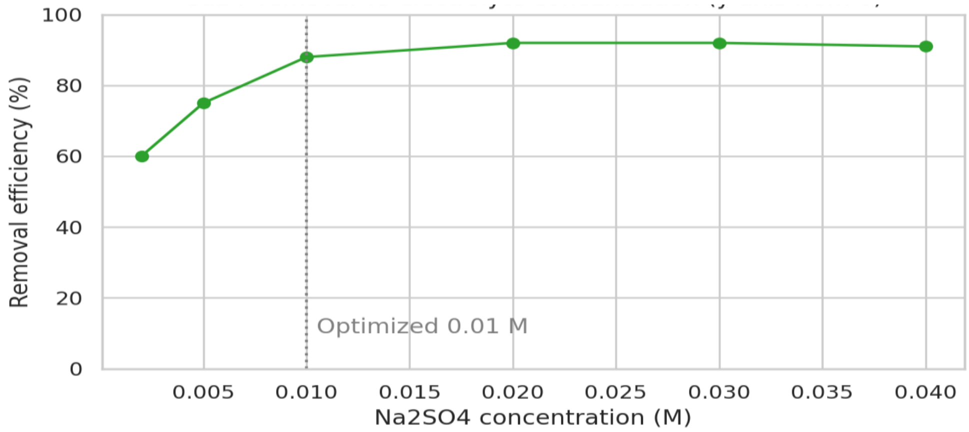


Fig. 11. Cd^{2+} Removal vs Electrolyte Concentration

3.5 Integration with Organic Contaminant Degradation

The degradation of phenanthrene proceeded concurrently with metal removal, confirming that the electrochemical system effectively addressed both contaminant types.

Parallel monitoring of phenanthrene degradation confirmed substantial removal within the same timeframe, with a 76 % decrease in GC–MS peak area by day 30 (Fig. 12). Transient detection of intermediates (hydroxy-phenanthrene, phthalic acid derivatives) indicated stepwise oxidation and eventual mineralization to CO_2 and H_2O. These intermediates are consistent with reported oxidative degradation pathways of PAHs (Huang *et al.*, 2017), where initial hydroxylation is followed by ring cleavage and final mineralization. Their subsequent disappearance suggests that the system is capable of driving degradation beyond partial oxidation, mitigating concerns about accumulation of toxic byproducts. The observed decay profiles align with the oxidative mechanism proposed in Equation (4), where ring hydroxylation precedes stepwise mineralization. This concurrent removal of organic (phenanthrene) and inorganic (Cd^{2+}) contaminants demonstrates the dual functionality of the PANI-based electroremediation system, providing both electrochemical oxidation and electrokinetic transport within a single reactor. Such integrated performance supports previous findings that conductive polymers can mediate mixed-contaminant removal through simultaneous redox coupling and electromigration (Gong *et al*., 2022; Li *et al*., 2023).

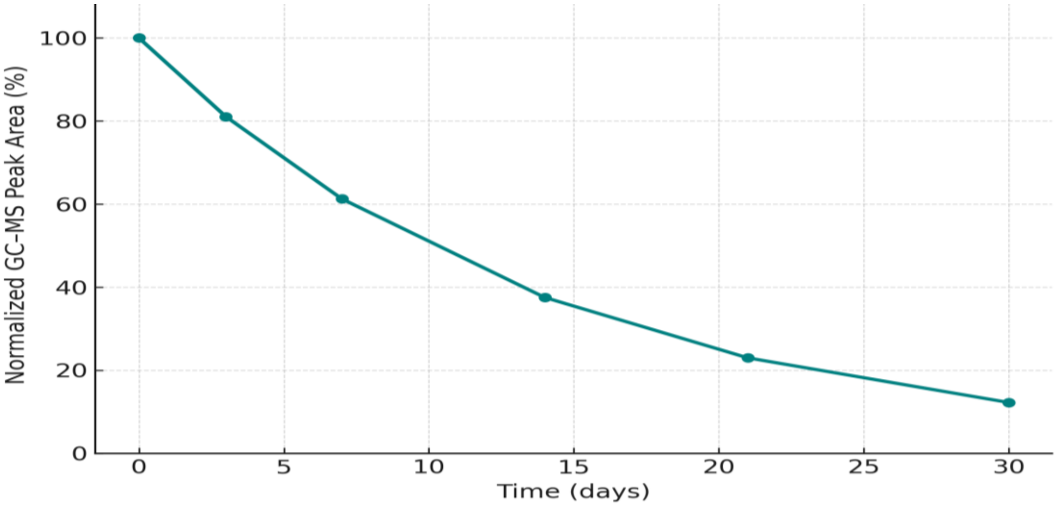


Fig. 12. Decrease in Phenanthrene Peak Area (m/z 178) over Remediation

3.6 Enhanced Electrochemical Performance of PANI Electrodes

The superior performance of the PANI electrodes can be attributed to their redox-active polymer structure, which provides pseudocapacitive charge storage and facilitates repeated electron exchange cycles. Compared with graphite, which relies on surface-limited reactions, PANI establishes a dynamic electroactive interface, maintaining higher steady-state current densities (1.5 mA cm^{-2}) compared to graphite (0.8 mA cm^{-2}). These findings are consistent with prior aqueous-phase studies where PANI-modified electrodes exhibited enhanced removal of phenols, dyes, and chlorinated organics (Zhou *et al*., 2019; Ahmed *et al*., 2021). Importantly, this study extends such benefits to soil matrices, which are more challenging due to limited conductivity, heterogeneous pore structures, and contaminant sorption.

3.7 Kinetic Modeling and Rate Analysis

To further interpret the contaminant removal dynamics, temporal decay profiles were fitted using the pseudo-first-order kinetic model (Equation 3).

The corresponding half-life ($t_{1/2}$) was obtained from:

$$t_{1/2} = \frac{ln(2)}{k} \qquad (5)$$

The degradation of Cd^{2+} followed a first-order kinetic model, as indicated by the linear relationship between $\ln(C_0/C_t)$ and time (Fig. 13). The rate constants (k) increased markedly across the electrode treatments: 0.003 day^{-1} (Control), 0.056 day^{-1} (Graphite), and 0.087 day^{-1} (PANI). These results correspond to half-lives ($t_{1/2} = ln2/k$) (Equ. 5) of approximately 231 days, 12.4 days, and 8.0 days, respectively, confirming that the PANI-coated electrodes accelerated the electrochemical removal process by enhancing charge transfer and ion migration efficiency. The bar chart clearly illustrates that while the Control system exhibited negligible Cd^{2+} attenuation, both electro-assisted treatments achieved substantial removal within 30 days, consistent with previously reported enhancement of metal ion transport under applied potential gradients. The slightly steeper kinetic slope for the PANI treatment suggests that polymer conductivity and redox activity improved the anodic dissolution and subsequent metal capture at the cathode surface.

Similarly, phenanthrene removal conformed well to first-order kinetics (Fig. 14), characterized by rate constants of 0.0051, 0.0201, and 0.0459 day^{-1} for Control, Graphite, and PANI electrodes, respectively. The corresponding half-lives were 136 days, 34 days, and 15 days, reinforcing that electrochemical oxidation, particularly with the conductive polymer electrodes, substantially enhanced organic contaminant degradation. The kinetic profiles in the bar plots reveal a progressive increase in $\ln(C_0/C_t)$ values with time, with the PANI treatment exhibiting the steepest slope, reflecting the most rapid oxidation. This enhanced degradation is attributed to the synergistic effects of (i) strong anodic potential facilitating hydroxyl radical generation, and (ii) the high electroactive surface area of the PANI film, which promotes electron exchange and catalytic oxidation of aromatic rings.

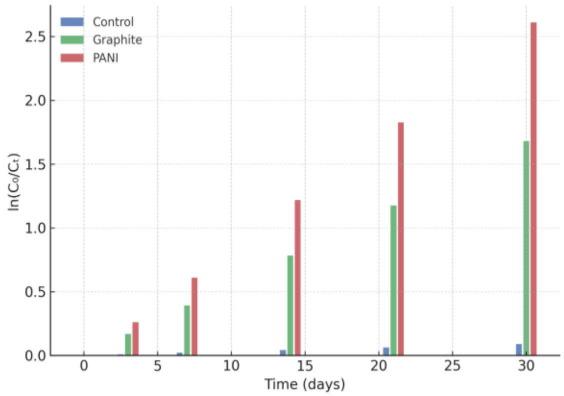


Fig. 13. Kinetic fit for Cd^{2+} Removal

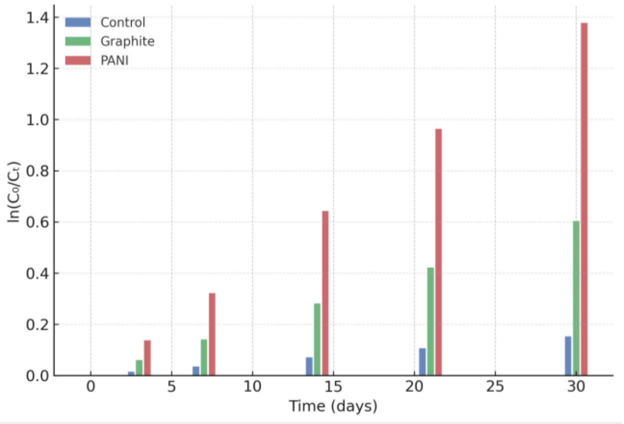


Fig. 14. Kinetic fit for Phenanthrene Removal

4.0 Conclusion

This study demonstrated that polyaniline (PANI)–coated electrodes provide an effective platform for the electrochemical remediation of soils contaminated with both heavy metals (Cd^{2+}) and hydrophobic organic pollutants (phenanthrene). The dual functionality of PANI enabled efficient Cd^{2+} removal via electrokinetic mobilization and adsorption, while simultaneously supporting phenanthrene degradation through direct electron transfer and indirect oxidation processes. The removal kinetics followed pseudo-first-order behaviour, while optimized operational parameters (2 V/cm, 0.01 M Na_2SO_4, 20% soil moisture) yielded high efficiency with minimal secondary effects. Monitoring with ICP–OES and GC–MS confirmed significant removal efficiencies (>80% for Cd^{2+} and >70% for phenanthrene) alongside the formation of identifiable oxygenated intermediates. Compared with conventional inert electrodes, PANI electrodes exhibited enhanced stability and reactivity, highlighting their promise for integrated, sustainable soil remediation. Future research should focus on scaling this approach, optimizing electrode configurations, and evaluating field-scale feasibility.

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