Analytical & Bioanalytical Electrochemistry

> 2024 by CEE www.abechem.com

Review

Recent Advances in Electrochemical Treatment Technology for the Remediation of Contaminated Soil

Shiva Dehghan Abkenar,^{1,*} Nazanin Khakipour,² and Iraj Alahdadi³

¹Department of Chemistry, South Tehran Branch, Islamic Azad University, Tehran, Iran ²Department of Soil Science, Savadkooh Branch, Islamic Azad University, Savadkooh, Iran ³Department of Agronomy and Plant Breeding Sciences, Faculty of Agricultural Technology (Aburaihan), College of Agriculture and Natural Resources, University of Tehran, Tehran, Iran

*Corresponding Author, Tel.: +98-9111174767 E-Mail: <u>dehghan54@yahoo.com</u>

Received: 14 January 2024 / Received in revised form: 13 March 2024 / Accepted: 15 March 2024 / Published online: 31 March 2024

Abstract- Soil contamination presents a significant hazard to both ecosystems and human wellbeing. Therefore, there is a need for cost-effective and environmentally friendly approaches to decontaminate polluted soils. Soil remediation involves the treatment of contaminated land to enhance soil quality, safeguarding public health and the ecosystem. Among the promising technologies for remediating soils contaminated with various substances, including inorganic, organic, and mixed contaminants, is electrochemical remediation. Electroremediation (ER) is an in-situ method that employs low direct electric current among electrodes fixed in contaminated soils to create an electric field. This review paper examines the advancements made in recent years in electrochemical remediation as an effective method for decontaminating polluted soil. The discussion begins by exploring electrochemical remediation, followed by the classification of contamination types in soil. The focus then shifts to the application of electrochemical treatment methods for removing heavy metals and organic contaminants from the soil. Additionally, the paper highlights recent progress in the exploration of integrating electrochemical treatment with other remediation techniques, such as phytoremediation and bioremediation.

Keywords- Soil contamination; Electrochemical remediation; Heavy metal; Organic contaminant, Electroremediation

1. INTRODUCTION

Soils and sediments serve as fundamental pillars for worldwide environmental sustainability, providing crucial resources to both humans and nature [1–4]. The anthropogenic influences resulting from land-use changes have variably influenced the ability of these geological features to uphold their basic functionalities. Key functions such as nutrient cycling, water preservation, providing of physical and chemical stability, storage, filtering, conversion of compounds, and supporting biodiversity are integral components of groundwater and food security [2,5]. A substantial proportion of global freshwater reserves (98-99%) is situated in the subsurface, with approximately 8-10 million km³ of freshwater either contained within or in direct contact with rock and soil [6].

In the context of a gradually populated and residential world, pollution stands out as a noteworthy task in the management of soil and groundwater resources [7]. Despite the critical nature of this issue, efforts to measure groundwater pollution remain limited [8], and the true extent of the problem is not well understood [9].

Mining, electroplating, and various industrial operations, along with practices such as sewage irrigation, the application of chemical fertilizers, and other agricultural processes, outcome in the substantial gathering of heavy metals and organic pollutants in the soil and/or sediment. These contaminants have the potential to bio-accumulate in living organisms, posing a threat to the health of plants, animals, and humans alike [10, 11].

Electrochemical remediation presents a capable avenue for addressing the contamination of fine-grained soils by various inorganic, organic, and mixed contaminants. This technology involves the usage of a direct-current (dc) electric field to the contaminated soil, driving the contaminants to move through the soil via a combination of electroosmosis, electromigration, and/or electrophoresis mechanisms. For a comprehensive understanding of these underlying electrokinetic phenomena in soil, detailed insights are available in the works of Yeung, 2010 and Yeung and Gu, 2011 [12,13].

One notable advantage of employing a dc electric field in this process is its superior effectiveness in transporting fluids through fine-grained soils compared to conventional hydraulic gradients [14]. Consequently, electrochemical remediation finds particular relevance in treating fine-grained soils characterized by low hydraulic conductivity and a substantial specific surface area. A comprehensive overview of key advancements and future research directions within this technology field can be found in Yeung's work [13].

However, it is crucial to recognize that the soil and chemical fluid system involved in electrochemical remediation constitutes a complex electrochemical system [15]. Throughout the remediation process of contaminated soil, numerous electrochemical reactions occur simultaneously[16]. Furthermore, the extensive specific surface area of fine-grained soil offers numerous sites for intricate interactions between the soil and contaminants. These interactions exhibit characteristics such as soil specificity, contaminant specificity, dynamism, reversibility,

and dependence on pH levels. The fusion of electrochemical reactions with these intricate soilcontaminant interactions significantly amplifies the intricacy of the electrochemical remediation process [13].

2. CONTAMINATION TYPES

Contamination types are considered in three groups:

- **Heavy Metal Remediation:** Methods designed specifically for the removal of heavy metals from soil, like lead, cadmium, and arsenic.
- **Organic Contaminant Remediation:** Techniques tailored to the degradation of organic pollutants, including hydrocarbons, pesticides, and volatile organic compounds (VOCs).
- **Mixed Contaminants:** Some methods are versatile and can address both heavy metals and organic contaminants simultaneously.

2.1. Heavy metal remediation

One of the features of remediating contaminated soils is the extraction of heavy metals from the affected soil or altering the presence of these metals in a manner that renders them non-hazardous to biological health. This process aims to eliminate heavy metal substances from the soil, ultimately restoring the soil's productive functionality [17]. Soil contamination by heavy metals is a significant ecological concern, originating from geogenic and anthropogenic sources such as mining, smelting, fossil fuel utilization, industrial emissions, waste dumping, and agricultural irrigation. The most toxic metal contaminants include Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Chromium (Cr), Mercury (Hg), Selenium (Se), Beryllium (Be) and Arsenic (As) [18–23]. Heavy metals, unlike organic contaminants, resist biodegradation and chemical degradation, leading to their long-term accumulation in soil [24]. This accumulation poses risks to the agricultural environment and human health, as metals are absorbed by plants and subsequently contaminate the food chain [24,25].

Remediating soil contaminated with heavy metals serves not only to diminish the bioavailability of metals in the soil and mitigate health risks to humans, animals, and plants but, more significantly, aims to eliminate metals from the contaminated soil [17].

Electrochemical treatment methods for heavy metal remediation in soil can be classified based on their underlying principles and mechanisms. Here are several categories of electrochemical methods used for heavy metal remediation: It is important to note that the selection of electrochemical process depends on factors such as the kind of heavy metal contaminants, soil characteristics, and project-specific requirements [23].

2.1.1. Electrokinetic remediation

The remediation of heavy metal-contaminated soils through electrokinetic technology is a widely accepted approach. Electrokinetic remediation, known for its effectiveness in metal mobilization and low repeated pollution, involves various technologies to boost metal removal efficiency in contaminated soil. An electrokinetic system comprises essential elements such as providing power to create electric fields, placing electrodes for generating these fields and introducing reactive mediums like electrolytes and other potential materials.

Among the diverse remediation techniques, electrokinetic remediation stands out due to its exceptional capacity for mobilizing metals and minimizing repeated pollution [26]. Numerous studies delve into the principles and fundamentals of electrokinetic remediation [27], wherein external power induces electromigration, electro-osmosis, and electrophoresis, influencing the movement of heavy metal ions. Electromigration emerges as the primary transport mechanism for these ions [28]. Electrokinetic remediation showcases effective removal performance in fine-grained soils with low hydraulic conductivity, proving applicable in both saturated and unsaturated soils, regardless of their type, pH, structure, organic content, or contaminant concentration [28,29].

The electrochemical procedure is capable of extracting heavy metals solely when they are found in a dissolved ionic state within the soil or adhered to colloidal particles. Various studies [13,30] highlight enhanced technologies employed for removing heavy metal ions from the soil. However, a comprehensive examination of the components of the electrokinetic system, including power for the electric field, electrodes, electrolytes, and other potential materials, remains a subject of limited exploration [23].

For example, in 2018, The method proposed for advanced remediation involves the utilization of potassium permanganate (KMnO₄) in conjunction with electrokinetics to address the low efficiency of Cr(III) removal in traditional electrokinetic remediation of chromiumcontaminated soil. Soils contaminated with chromium residues typically exhibit a higher proportion of trivalent chromium [Cr(III)]. In this study, a DC voltage of 1 V cm⁻¹ was applied while introducing KMnO4 into the cathode to enhance the remediation process. The experiments, conducted over a 96-hour period, focused on simulated Cr(III)-contaminated Kaolin and actual chromium residue-contaminated soils sourced from a Chinese chemical factory. Results demonstrated a significant improvement in total chromium [Cr(T)] removal efficiency through the KMnO₄ oxidation-electrokinetic advanced remediation method. The Cr(T) removal rates were notably higher in groups with KMnO₄ oxidation, reaching 78.4% and 42.6% for simulated Cr(III)-contaminated Kaolin and chromium residue-contaminated soils, respectively. In comparison, the control groups without KMnO₄ oxidation exhibited lower removal rates of 32.4% and 20.9% for the respective soil types. The enhancement in Cr(T) removal rates correlated with the concentration of KMnO₄, indicating a positive relationship. Under the influence of the direct electric field, MnO₄⁻ introduced in the cathode migrated towards the anode. Simultaneously, Cr(III) positive ions moved through the soils towards the cathode. Some Cr(III) ions underwent precipitation on the soils during migration, while others were oxidized to hexavalent chromium [Cr(VI)] ions during the migration of KMnO₄. The Cr(VI) negative ions migrated towards the anode at a faster rate than Cr(III) ions in the soils, effectively controlling the precipitation of Cr(III) ions and improving overall chromium removal efficiency [31].

One of the vital features for the remediation of contaminated soils is a decrease in metal bioaccessibility. In 2023 wang et al. studied how to clean soil contaminated with uranium using electrochemical leaching. They used a mix of citric acid and ferric chloride as the electrolyte for the electrokinetic remediation of uranium-contaminated soils. The results presented that they removed up to 70.45% of uranium, which was more effective than using leaching alone. After the cleaning process, the amount of uranium and other metals that could be absorbed was much lower, and the overall stability of metals in the soil improved, especially near the positive electrode (anode). The levels of bioaccessible uranium, manganese, lead, and zinc were connected to their respective concentrations, the soil's acidity, and the shapes of the metals in the soil [32].

Converting hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) in contaminated soil stands as an inexpensive strategy to mitigate the toxic effects of Cr(VI) on the ecosystem. Cr(III) is recognized for its essential role in trace concentrations for both plants and animals, while Cr(VI) is identified as a human carcinogen due to its facile penetration of cell walls, exerting deleterious effects within the cell [33]. The redox status of chromium significantly influences its chemical behaviors and biological toxicity. In a study, in 2021 an innovative electrokinetic remediation (EKR) system incorporating UV light was investigated to defeat the energy barrier and catalyze the reduction of Cr(VI) from the surface soil near the anodic reservoir. The presence of natural organic substances and minerals in the polluted soil acted as electron donors and facilitators for the photo-reduction of Cr(VI), eliminating the necessity for extra chemical agents. The anolyte following UV/EKR exhibited minimal residual Cr(VI) compared to conventional EKR. The substantial decrease in Cr(VI) had a positive impact on the effectiveness of Electrokinetic Remediation (EKR) in the soil adjacent to the anodic reservoir. This reduction mitigated the adverse mass flux of Cr(VI) resulting from electroosmosis advection and concentration diffusion. The primary pathways for the photoreduction of Cr(VI) in this system appear to be largely influenced by ligand-to-metal charge transfer, specifically through photocatalytic cyclic reduction facilitated by Fe(III)/Fe(II) complexes on mineral surfaces and in soil pore fluid. Additionally, there is evidence of photoinduced decomposition of chromate ester. These findings confirm that UV/EKR serves as an environmentally friendly and cost-effective approach for remediating Cr (VI)-contaminated soil [34].

A new study in 2024, investigated the remediation of arsenic and cadmium-contaminated soil in karst areas through the application of electrification and citric acid approaches as represented in Figure 1. Higher concentrations of citric acid were found to enhance the dissolution of arsenic and cadmium in the soil. Electrification further facilitated the breakdown of cadmium and arsenic in the soil through the citric acid system. The experimental results indicated removal rates of 89.19% for oxidizable arsenic, 48.97% for acid-extractable arsenic, 60.88% for oxidizable cadmium, and 87.87% for acid-extractable cadmium. In karst environments, alkaline conditions favored the desorption and migration of arsenic, while high calcium conditions inhibited arsenic dissolution and promoted cadmium dissolution. The study revealed that cadmium predominantly existed in the forms of Cd^{2+} and Cd-Citrate-, while arsenic existed as $H_2AsO_4^-$ and H_3AsO_4 in acidic environments, and as $HAsO_4^{2-}$ and $H_2AsO_4^-$ in alkaline conditions [35].



Figure 1. The schematic diagram of the Electrokinetic system [35]

In another investigation conducted in 2024, a novel UV/EKR system, integrating electrokinetic remediation (EKR) technology with ultraviolet (UV) photoreduction, was employed to investigate the enhanced reduction of Cr (VI) in real contaminated soil using oxalic, malic, and tartaric acids. The results revealed that the inclusion of UV radiation resulted in the removal of 99.49% of Cr (VI) from the anolyte and significantly boosted the removal efficiency of high-concentration Cr (VI) in the near anode soil layer by 14.83% compared to conventional EKR methods. Among the three acids tested, malic acid exhibited superior performance by alleviating clogging from precipitates, providing more photocatalyst Fe (III), and reducing the retention of the reduction product Cr (III) in the soil. Consequently, malic acid achieved removal rates of 90.38%, 83.82%, and 27.14% for water-soluble, weakly bound,

and strongly bound Cr(VI), respectively, in the near-anode soil layer. The synergistic combination of organic acids with the UV/EKR technique demonstrated high compatibility, offering a promising solution to address the suboptimal reduction efficiency of Cr(VI) in practical soil applications within the realm of EKR. This innovative approach introduces fresh perspectives for the in-situ remediation of chromium-contaminated soil [36].

In certain instances, electrokinetic remediation alone may not yield soil conditions that meet acceptable environmental standards. Recognizing this limitation, researchers and environmental practitioners have explored the synergistic integration of electrokinetic processes with other remediation technologies to bolster the removal of heavy metals from contaminated soil. Notably, coupling electrokinetic remediation with permeable reactive barriers (PRB), soil washing, bioremediation, and phytoremediation has proven to be effective. This combination harnesses the strengths of both methods, where the electrokinetic process mobilizes contaminants, and the permeable reactive barriers further intercept and treat these contaminants, collectively enhancing remediation efficiency. Additionally, the integration of electrokinetic remediation with soil washing, bioremediation, and phytoremediation has showcased significant promise. In these approaches, electrokinetics serves as a catalyst, facilitating the mobilization of heavy metals, while soil washing, bioremediation, and phytoremediation contribute complementary mechanisms for capturing, degrading, or extracting contaminants from the soil matrix. This collaborative utilization of diverse remediation strategies reflects a comprehensive and tailored approach to addressing soil contamination, ensuring a more thorough and sustainable restoration of soil quality to meet environmental standards [23].

2.1.2. Electrooxidation

In this method, heavy metals are oxidized at the anode, converting them into less toxic or insoluble forms. The anode undergoes oxidation reactions, promoting the breakdown or transformation of heavy metal contaminants. In a study conducted in 2020, a hybrid sludge conditioning approach involving electrooxidation and the addition of Fe(II) was employed to efficiently eliminate heavy metals from both sewage and industrial sludge. Simultaneously, this method promoted the dewatering and stabilization of the sludge. The treatment, which involved introducing 82 mg/g of Fe(II) and lasting for 4.5 hours, resulted in significant removal rates. Specifically, Cu removal rates were 72.95% (sewage sludge) and 78.49% (industrial sludge), Zn removal rates were 66.29% (sewage sludge) and 84.26% (industrial sludge), and Pb removal rates were 36.52% (sewage sludge) and 36.99% (industrial sludge). This treatment led to a reduction in system pH to 2.33 and 2.98, coupled with an increase in oxidation-reduction potential (ORP) values to 435.90 mV and 480.60 mV in sewage sludge and industrial sludge samples, respectively. These altered conditions were conducive to the efficient desorption and dissolution of heavy metals from the sludge structures. Simultaneously, the process facilitated the degradation of organic compounds complexed with heavy metals.

Furthermore, the hybrid conditioning process demonstrated notable dewatering performance, achieved through the effective electrochemical disintegration of sludge flocs and the coagulation of sludge particles through the generation of Fe(III) via electrooxidation. The vital role in pathogen inactivation was played by the significantly acidic and oxidative conditions generated through the enhanced electrooxidation process [37].

2.1.3. Electrochemical reduction

Reduction reactions occurring at the cathode play a crucial role in transforming metal ions into states that are either less mobile or less toxic. Cathodic reduction facilitates the conversion of metal ions into their elemental forms or less mobile counterparts. In a study conducted in 2022, a novel approach was proposed to investigate the potential enhancement of heavy metal removal efficiency by combining chelating agent washing and electrochemical reduction. The research delved into the removal performance, mass transport mechanisms, and economic benefits associated with both the combined strategy and individual soil washing. The combination technique demonstrated a significant improvement in the removal efficiency of heavy metals. The synergistic enhancement effect observed was attributed to the chelating agent's chelating ability and regeneration capacity. The research was centered on investigating the effectiveness and mechanisms involved in the removal of Cadmium (Cd) and Lead (Pb) under various current conditions by employing a combination of EDTA washing and electrochemical reduction. The amalgamation of these techniques demonstrated a significant enhancement in the removal efficiencies of Cd and Pb, ranging from 13.37% to 15.24% and 14.91% to 27.05%, respectively, in comparison to using EDTA washing alone.

An analysis of sequential extraction unveiled the pivotal role of the reducible fraction in improving the efficiency of metal removal. The percentage of metal removed exhibited an increase with higher current values and EDTA concentrations. Although the differences were not statistically significant (p > 0.05), the pulse current mode proved more effective in eliminating Cd and Pb compared to continuous current. Moreover, pulse current successfully eliminated the cathodic hydrogen evolution reaction, leading to additional deposition of heavy metals at the cathode.

The combined method demonstrated an enhanced removal efficiency equivalent to EDTA renewal in the suspension and the cathodic reduction reaction. The most favorable results were achieved within a 48-hour timeframe using a pulse current mode of 32 minutes on/16 minutes off, a current of 32 mA, and an EDTA concentration of 10 mM. This treatment resulted in the removal of 47.56% of Cd and 77.00% of Pb from the soil [38].

2.1.4. Electrocoagulation

Over the last decade, electrocoagulation (EC) has occurred as a capable treatment approach for heavy metal wastewater [39,40]. This method is known for its excellent removal efficiency, absence of secondary pollution, and minimal sludge production. In the EC process, coagulants are spontaneously generated in situ through the dissolution of metal ions, demonstrating a robust adsorption capacity for pollutants. Nevertheless, the conventional EC process faces a significant challenge – the passivation of aluminum electrodes.

In this process, a passive film forms on the electrode surface, hindering the formation and mass transfer of Al^{3+} in the solution. This passivation leads to increased power consumption and reduced efficiency [41]. Currently, three main methods have been proposed to address the formation of passive films on electrodes: alternate pulsed current, ultrasound, and chloride addition.

Alternate pulsed current (APC) efficiently averts passivation in aluminum electrodes by altering the passive layer developed during the aluminum-electrocoagulation (Al-EC) process [42]. However, the frequent exchange of electrode polarity may adversely affect the lifespan of the power supply. Another method involves the use of ultrasound during the EC process. The ultrasonic process applies high pressures to disrupt passive films through cavitation at the solid-liquid interface of anodes [43]. Nevertheless, the use of ultrasound may break down flocs, potentially reducing removal efficiency [44]. The simplest and most widely employed technique is the addition of chloride in the EC process. Chloride contributes to the rupture or reduction of the protective passivation film due to its strong penetration or adsorption [45, 46]. Cl^- ions adsorbed on the surface of the Al anode react with Al species in the oxide film, resulting in the chemical dissolution of the passivation film [45].

In a 2023 study, Zeng et al. highlighted the efficacy of combining electrocoagulation (EC) and electrooxidation (EO) for immobilizing phosphorus and heavy metals, as well as oxidizing ammonium and toxic organic substances. The utilization of an integrated mixed metal oxide (MMO)/Fe anode system facilitated the efficient removal of ammonium and phosphorus from overlying water, achieving a remarkable disappearance of 99% of 10 mg/L NH₄⁺-N and 95% of 10 mg/L P within 15 and 30 minutes, respectively. In comparison to control setups involving single Fe anode or single MMO anode systems, the dual MMO/Fe anode system exhibited a significant enhancement in phenanthrene removal and facilitated the transformation of Pb and Cu from mobile to immobile species. Notably, concentrations of Pb and Cu in toxicity characteristic leaching procedure extracts were reduced by 99% and 97% following an 8-hour operation. Further assessments using four real polluted samples demonstrated substantial reductions in the acid-soluble fraction of Pb and Cu (30%-31% for Pb and 16%-23% for Cu), along with notable decreases in total organic carbon and NH_4^+ -N by 56%–71% and 32%–63%, respectively. The proposed mechanism attributed the outstanding performance of the cotreatment to in situ electrogenerated Fe(II) at the Fe anode and active oxygen/chlorine species at the MMO anode. The results strongly indicate that the EC/EO method represents a potent technology for the in-situ remediation of sediments contaminated with diverse pollutants [47].

In a study conducted by Maja Pacieja, the effectiveness of electrocoagulation employing an aluminum sacrificial anode was examined for its ability to separate chelating agents and heavy metals from a washing solution obtained after leaching lead (Pb) at 3200 mg kg⁻¹, zinc (Zn) at 1100 mg kg⁻¹, and cadmium (Cd) at 21 mg kg⁻¹ from contaminated soil using EDTA. During the electrochemical process, the sacrificial anode corroded, releasing Al³⁺ ions, which acted as a coagulant, leading to the precipitation of chelant and metals. Applying a constant current density ranging from 16 to 128 mA cm⁻² between the aluminum anode and stainless-steel cathode resulted in the removal of up to 95% of Pb, 68% of Zn, and 66% of Cd from the soil washing solution. Following treatment, approximately half of the initial EDTA persisted in the washing solution, with up to 16.3% of EDTA being adsorbed on the Al coagulant and precipitated, while the remaining EDTA underwent degradation through anodic oxidation.

In another test conducted on a laboratory scale, soil was leached with 40 mmol EDTA per kg of soil, and the washing solution (post-electrocoagulation) was reused in a closed loop. This process resulted in the removal of 53% of Pb, 26% of Zn, and 52% of Cd from the soil. The discharge solution exhibited clarity and colorlessness, with a pH of 7.52, containing 170 mg L^{-1} Pb, 50 mg L^{-1} Zn, 1.5 mg L^{-1} Cd, and 11 mM EDTA [48].

The Soil Flushing Solution (SFS) resulting from the remediation of soil contaminated with Cr(VI) is a type of non-industrial wastewater containing Cr(VI). The need for on-site treatment of SFS imposes stringent requirements for operational simplicity and transportability. A study in 2017 presents an on-site, application-oriented continuous electrocoagulation (EC) system designed for SFS treatment. Through an innovative strategy, a series of electrochemical, redox, and precipitation reactions are harnessed to generate an acidic area for Cr(VI) reduction by Fe²⁺ and a basic area for Cr_xFe_y(OH)_z precipitation. The treated SFS exhibited concentrations of Cr(VI), total Cr, and total suspended solids below 0.03 mg.L⁻¹, 0.16 mg·L⁻¹, and 39 mg.L⁻¹, separately, meeting typical environmental discharge regulations. Stirring intensity experiments revealed the necessity of stirring to reduce Cr(VI)/Total Cr in sediments. Comparing desorption kinetics among treated SFS and tap water indicated that the Cr(VI) desorption efficiency with treated SFS is a little larger than with fresh tap water, satisfying the necessity for SFS reuse [49].

2.1.5. Membrane Electrochemical Remediation (MER)

Membrane Electrochemical Remediation (MER), also known as electrodialytic remediation, is acknowledged as a highly effective technique for extracting heavy metals from various porous media, including soil, sediment, fly ashes, and mine tailings [50,51]. In MER, an electric field is applied across the soil matrix, causing ions in the soil to migrate under its influence. The process utilizes membranes to selectively transport specific ions, leading to the separation and removal of contaminants from the soil. This technology is effective in extracting heavy metals and other charged contaminants, facilitating their migration toward electrodes for collection or further treatment.

The advantages of MER include its capability to target and remove specific contaminants, the potential for in situ remediation without excavation, and its applicability to various soil types. However, factors such as the type of contaminants present, soil characteristics, and the potential for secondary reactions during the remediation process should be considered.

As with any remediation technology, the effectiveness of MER can vary depending on sitespecific conditions. Its application should be carefully evaluated based on the nature of the contamination and the site's characteristics. The Membrane Electrochemical Remediation (MER) system, initially conceptualized as a three-compartment cell segregated by an anionexchange membrane (AEM) and a cation-exchange membrane (CEM) [52], operates within a direct current (DC) electric field produced by an anode and a cathode.Within the middle suspension compartment, soluble cationic and anionic contaminants are permitted to traverse the CEM and AEM, respectively, concentrating in the electrode compartments [52–54]. The continuous generation of H⁺ ions resulting from the polarization (water splitting) effect on the AEM leads to the ongoing acidification of the soil suspension in the middle compartment during MER. This acidification, in turn, facilitates the dissolution of metal cations from the insoluble oxidized state within soil particles [55].

In a 2020 study conducted by Song et al., a soil contaminated with multiple metals (Cr, Cu, and Ni) sourced from a polluted electroplating site served as the experimental substrate. Laboratory experiments involving three current density gradients and two MER strategies (anodic and cathodic processes) were executed to treat the soil suspension. The MERs based on the anode process exhibited maximum removal efficiencies for Cr, Cu, and Ni at 79.5%, 86.2%, and 85.0%, respectively, in contrast to 27.5%, 72.5%, and 65.9% for the cathode process. Risk assessment findings indicated a diminished environmental risk to the soil after employing MER based on the cathode process compared to the anode process. The study underscores the evolving role of MER based on the cathode process as a robust soil remediation strategy, showcasing its notable simultaneous remediation capabilities for soil heavy metals and leaching materials, with evident advantages in terms of environmental friendliness and economic effectiveness.

The conventional two-compartment strategy employed in Membrane Electrochemical Remediation (MER) for dissolving metals through acidification often results in significant soil pH reduction, rendering the materials less suitable for reuse. Chelating agents offer an alternative approach to dissolve various toxic metals in soil without causing substantial alterations to the soil pH. Ethylenediaminetetraacetic acid (EDTA), a widely utilized chelating agent, has proven successful in enhancing various soil remediation methods, including electrokinetic remediation [56], soil flushing [57], and phytoextraction [10], by forming Me-EDTA complexes with various metals (Me). In a novel method introduced for ethylenediaminetetraacetic acid (EDTA)-enhanced electrokinetic (EK) remediation, the combination of dual cation-exchange membranes and circulation methods was applied to address an aged electroplating soil contaminated with chrome (Cr), copper (Cu), and nickel (Ni). Three laboratory-scale experiments were performed using electrokinetics (EK): T1,

employing the conventional EK method; T2, utilizing the conventional EK method enhanced with EDTA; and T3, employing the EDTA-enhanced EK method with assistance. The results revealed that the removal of Cu and Ni in T3 was 3–10 times higher than in T1 and T2. Despite the small removal of Cr (total) in all experiments due to the high content of Cr (III), T3 resolved the metal accumulation issue observed in T1 and T2. Additionally, the highly acidified area (pH < 4) was reduced from 80% in T1 and T2 to only 20% in T3. The findings of T3 highlighted that the chelating effect of EDTA demonstrated a superior ability to dissolve oxidizable Cu and Ni in the soil compared to the acidification effect. The assessment of toxicity verified that the soil subjected to T3 treatment exhibited reduced adverse effects on a luminescent bacterium (Photobacterium phosphoreum T3), corresponding with a trend toward neutralization of soil pH after treatment. This research not only offers a novel, environmentally friendly method for heavy metal removal from the soil but also elucidates the root causes behind the challenges of low removal efficiency and high accumulation observed in traditional EK processes [58].

2.2. Organic contamination remediation

Electrochemical treatment methods for organic compound remediation in soil can be classified based on their mechanisms and approaches to degrading or removing organic contaminants. Here are several categories of electrochemical methods used for organic compound remediation

The process of electrochemical remediation (ER) for soil involves applying low potentials between a pair of electrodes to generate an electric field (E) in the contaminated area.

In a 2023 study, extremely low electric field values ($E \le 0.25 \text{ V cm}^{-1}$) were utilized for ER on contaminated kaolin as represented in Figure 2. Phenol was chosen as the typical harmful organic compound, and kaolin served as a model clay with reproducible, low buffering, and low permeability characteristics. The study delved into various factors, such as electrode nature, treatment time, current type, electric field strength, and the supporting electrolyte's nature, meticulously examining their influence on the process's performance. The key finding was that employing a very low electric field strength (0.15 V cm⁻¹) enabled the simultaneous desorption, mobilization, and in-situ degradation of phenol. The most substantial phenol removals, reaching around 80% and 90% from kaolin under direct and sinusoidal electric fields, respectively, were achieved using compact graphite electrodes in the occurrence of Na₂SO₄ in the kaolin. In this study, phenol extraction from the kaolin samples involved consuming pure methylene chloride. About 1.0 ± 0.05 g of the completely mixed treated clay sample was combined with 6.5 g of methylene chloride in a Teflon-sealed glass vial, subjected to sonication for 30 min, and centrifuged at 4000 rpm for 30 min. Each kaolin sample underwent three extractions to certify complete phenol extraction. The supernatant was filtered through a Teflon membrane and subsequently analyzed using HPLC [59].



Figure 2. The schematic representation of electrochemical remediation of spiked soil [59]

In a recent 2024 study, researchers conducted an investigation into the electrochemical remediation of kaolin deliberately contaminated with a mixture of five alkanes (C12H26, C13H28, C14H30, C16H34, C18H38), collectively referred to as C12-C18. Kaolin was chosen as the ideal model due to its reproducibility, low buffering capacity, and low permeability, while the C12- C_{18} mixture represented a hazardous model for petroleum hydrocarbon compounds. The study delved into various operational factors, such as electric field intensity, technology type, and the presence of supporting electrolytes. The findings indicated that employing low electric field intensities could simultaneously mobilize and in situ degrade the C12-C18 mixture, with a notable observation that the efficiency of remediation (R) increased as the alkane chain length decreased. Specifically, the study demonstrated that utilizing an electric field of approximately 0.50 V cm⁻¹ allowed for achieving a total removal of C₁₂-C₁₈ of around 70% after 96 hours. Moreover, the research revealed that the addition of sodium chloride had a positive impact on the process's performance. The inclusion of NaCl led to a substantial improvement in the removal efficiency of C₁₂-C₁₈, increasing from 61% to 83%. This highlights the enhancing effect of sodium chloride in optimizing the electrochemical remediation process for the specified mixture of alkanes [60].

Another study explores the viability of combining electrokinetic remediation and electrochemical oxidation for polluted soil containing organic dyes, specifically Reactive Black 5 (RB5) dye spiked in kaolinite. Organic dyes constitute a significant source of environmental contamination and are consequently deemed hazardous to the environment. The majority of these industrial dyes are not only toxic but also, unfortunately, exhibit considerable stability and mutagenic properties [61-63]. The approach involves employing soil electrokinetic treatment alongside liquid electrochemical oxidation to achieve comprehensive remediation and organic pollutant degradation. Effective RB5 removal from kaolinite was achieved through electrokinetics, with outcomes dependent on operating conditions. Complete

RB5 removal was attained using K₂SO₄ as the processing fluid, optimizing desorption from the kaolinite matrix, and operating with pH control at 7 on the anode. This created an alkaline environment, ionizing RB5, and facilitating migration toward the anode for electrochemical oxidation. The optimized conditions remarkably reduced electric power consumption (56 kW/mg of removed dye) compared to unenhanced electrokinetic processes. Separate electrochemical decolorization tests confirmed the efficiency of K₂SO₄ in the process, with a linear relationship between its concentration and decolorization rate. The proposed environmentally friendly in situ method combines soil electrokinetic treatment and liquid electrochemical oxidation for total dye degradation. The study focuses on electrokinetic remediation of kaolin polluted with RB5 and its degradation through electrochemical oxidation [64].



Figure 3. The schematic representation of electrokinetic remediation coupled with biochar in a permeable reactive barrier [65]

In 2022, Coconut shell biochars produced through oxygen-free pyrolysis between 300-700°C were integrated into a permeable reactive barrier (PRB) for electrokinetic remediation (EK) to eliminate 2,4,6-trichlorophenol (2,4,6-TCP) from soil as represented in Figure 3. Results demonstrated that using biochar in the PRB doubled the removal of 2,4,6-TCP compared to PRB without biochar. Orthogonal tests indicated that voltage input, rather than biochar pyrolysis temperature, primarily influenced TCP removal during the EK-PRB process. Optimal TCP removal exceeded 55% under conditions of 2 V cm⁻¹ voltage, 700°C pyrolysis temperature, and 40 mg L⁻¹ initial TCP concentration. Biochar played three key roles during EK remediation: enhancing electroosmotic flow (EOF) to accelerate TCP migration in soil,

moting electrochemical degradation of TC

directly removing TCP via adsorption, and promoting electrochemical degradation of TCP. Biochar from higher pyrolysis temperatures was preferred for coupling with EK due to its superior ability to enhance EOF and pollutant adsorption, making it effective for removing organic contaminants [65].

2.2.1. Volatile Organic Compounds (VOCs)

Aromatic hydrocarbons (AHs) are extensively released into the natural environment through the incomplete combustion of organic materials such as oil, petroleum products, gas, coal, and wood. Structurally, AHs can be categorized into monocyclic or polycyclic hydrocarbons, with a notable subset being polycyclic aromatic hydrocarbons (PAHs). Among monocyclic AHs, special emphasis is placed on BTEX (Benzene, Toluene, Ethylbenzene, and Xylene). Conversely, PAHs are characterized by fused benzene rings and are further divided into light and heavy PAHs based on the number of benzene rings in their structure. Those with up to four benzene rings fall into the light PAH category, while those with more than four rings are classified as heavy PAHs [66,67]. PAHs exhibit lipophilic properties, are minimally volatile, and demonstrate near-insolubility in water. Additionally, the lipophilicity of PAHs correlates directly with the number of rings in their structure. Most PAHs are not synthesized directly for commercial purposes; instead, certain PAHs like Acenaphthene, Anthracene, Fluoranthene, Fluorene, Phenanthrene, and Pyrene are utilized as precursors in the synthesis of pesticides, pharmaceuticals, dyes, pigments, plastics, and other industrial applications [68,69]. Advanced oxidation processes (AOPs) stand out as highly effective methods for eliminating organic contaminants, with in situ generated reactive species playing a crucial role in degradation. These processes swiftly remove a wide range of pollutants, including dyes, pesticides, endocrine disruptors, and emerging contaminants, achieving complete mineralization within a short timeframe. AOPs offer promise for transforming target compounds into less or non-toxic forms and eventually achieving complete mineralization [70-72]. This advantage is harnessed for degrading polycyclic aromatic hydrocarbons (PAHs) in both aqueous media and contaminated sites. The physicochemical properties of PAHs, particularly solubility and hydrophobicity, increase with the number of aromatic rings [73]. Notably, derivatives of PAHs feature various functional groups like -NO₂, -NH₂, -OH, -COOH, SO₃H, etc. Consequently, their degradation in AOPs relies on these functional groups, guiding reactive species to specific positions on the aromatic ring. Future studies exploring their reactions with reactive species and subsequent degradation hold significant interest [68,69].

Herbicides and pesticides have been extensively employed over the past decades to maintain the quality and quantity of agricultural crops, addressing the increasing demand for global food production. However, these synthetic organics exhibit high stability under mild conditions, posing challenges for effective degradation in traditional wastewater treatment facilities. In the quest for advanced oxidation processes to eliminate them, electrochemical technologies have emerged at the bench scale as potentially potent treatments. Some studies explore nine treatment methods, encompassing single techniques such as anodic oxidation, anodic oxidation with electrogenerated H₂O₂, homogeneous and heterogeneous electro-Fenton, photoelectron-fenton, solar photoelectro-Fenton, and photoelectrocatalysis. Additionally, combined approaches involving hybrid and sequential processes have been thoroughly examined [74,75]. The treatment of soils for herbicide removal involves the initial extraction of herbicides with surfactants, leading to the production of a flushing effluent for subsequent remediation [76]. Among various techniques developed for herbicide removal from wastewaters and soils, advanced oxidation processes (AOPs) are considered the most efficient treatments. AOPs involve the in-situ generation of hydroxyl radicals (OH), a potent oxidant capable of non-selectively reacting with organic compounds, leading to their mineralization through hydroxylation and dehydrogenation reactions [77].

Different AOP treatments for herbicide wastewaters include UV/H₂O₂ photolysis, photocatalysis with TiO₂/UV or ZnO/UV, pulse electric discharge plasma, gamma irradiation, sulfate radical-based catalysts, sonolysis, and O₃-based AOPs [78]. Electrochemical AOPs (EAOPs), such as anodic oxidation (AO) and electro-Fenton, have demonstrated superior performance in herbicide degradation [79,80].

2.2.2. Anodic Oxidation

Anodic oxidation (AO), a popular EAOP for wastewater treatment, depends on the nature of the anode material, determining the type and power of the generated oxidants. Active anodes, like Pt and dimensionally stable anodes (DSA), lead to selective transformation of organics into biodegradable by-products, while non-active anodes, such as metal mixed oxides (MMO), result in complete mineralization of organics to CO₂ and inorganic ions. The AO process involves direct electron transfer to the anode or mediated oxidation with species generated from water discharge, leading to partial or total decontamination. two extreme ideal anodes are proposed to explain their oxidation power: active anodes yield electrochemical conversion with selective transformation, while non-active anodes act as inert electrodes with low interaction and complete mineralization. The water discharge to O₂ involves the initial formation of physiosorbed OH as an intermediate. Active anodes oxidize M(OH) to "active oxygen" MO, attacking organics until carboxylic acids are formed. In contrast, non-active anodes lead to the electrochemical combustion of organics into CO₂.

The competition between desired reactions and parasitic reactions, such as the direct oxidation of M(OH) to O_2 , its dimerization to H_2O_2 , or its reaction with H_2O_2 to form the weaker oxidant hydroperoxyl radical, influences the overall effectiveness of the AO process. While other weaker oxidants like ozone can be produced, the strongest M(OH) is the primary reactive oxygen species pre-eminently attacking organic pollutants [74,81].

2.2.3. Homogeneous and Heterogeneous Electro-Fenton

The homo-electro-Fenton (homo-EF) process has been proposed as an improvement over anodic oxidation (AO), utilizing the oxidation potential of H_2O_2 generated at the cathode

through the catalytic action of soluble iron ions. This dual approach offers significant advantages, including the in situ electrogeneration of H_2O_2 , eliminating the need for hazardous transport and storage. Additionally, homo-EF demonstrates faster organic degradation compared to conventional Fenton treatment, requiring a smaller quantity of added Fe²⁺ since it is regenerated at the cathode. Furthermore, potential total mineralization is achievable with relatively low electric consumption [82].

However, certain drawbacks associated with homo-EF include its limitation to acidic wastewaters (pH 2-4), the substantial use of chemicals for effluent acidification or neutralization before disposal, and the necessity for sludge treatment post-neutralization, leading to increased operational costs. To address these challenges, the hetero-electro-Fenton (hetero-EF) process has been developed, operating at neutral pH using insoluble iron catalysts or cathodic materials with iron [83].

Recent research has focused on both homo-EF and hetero-EF to demonstrate their effectiveness in herbicide remediation at the laboratory scale. The fundamentals of the process involve H₂O₂, a green chemical and weak oxidant, which can be activated in acidic matrices by catalytic metallic ions, with the popular combination being H₂O₂ and Fe²⁺ known as Fenton's reagent. This produces Fe³⁺ and homogenous OH as strong oxidants for organics. In the homo-EF process, H₂O₂ and added Fe²⁺ are continuously generated at a carbonaceous cathode with a high surface area, making it more powerful than conventional Fenton treatment. The reduction of O₂ to H₂O₂ occurs at the surface of immersed cathodes, such as carbon felt [84], through a two-electron reaction (E = 0.68 V/SHE) [81].

2.2.4. Electrochemical Cleaning of Oil Contaminated Soil

Petroleum hydrocarbons (PHs) are widely utilized in industries and energy production but can become soil pollutants, posing significant threats to living organisms. Traditional chemical treatment methods for soil remediation are often expensive and environmentally unfriendly. To address these issues, researchers are exploring new, eco-friendly strategies based on risk analysis. The focus is on bioremediation, specifically using microorganisms, with Nextgeneration sequencing (NGS) technologies monitoring contaminated sites. Nanotechnology shows promise for effective soil remediation, with an emphasis on bio-electrochemical systems utilizing electrochemically active microorganisms, providing an eco-friendly and tailored approach to sustainable remediation technologies [85]. As outlined by the Environmental Protection Agency (2005), accidental leaks from oil and gas tankers, mishaps during loading, transportation, storage, and distribution, or oil spills can result in environmental pollution. Fossil-based petroleum hydrocarbons (PHs) are generally classified into aliphatic, heterocyclic, and aromatic categories. The concentration of PHs in the environment has risen due to the widespread use of various petrochemicals and the generation of related industrial waste products and effluents. PHs have been identified as pollutants in soil, posing an emerging threat to the environment, and are known to be neurotoxic and carcinogenic to humans [86–88].

The impact of petroleum hydrocarbons on the environment and soil depends on their chemical and physical characteristics, with various components affecting soil properties through processes like adsorption, biodegradation, and leaching [89]. Contaminated soil can lead to adverse effects on soil fertility, physical and chemical properties, potentially affecting the food chain and causing toxicity in humans. Agriculture soil, crucial for providing food and maintaining ecosystem balance, faces negative consequences from soil contamination [90].

In a study conducted by Al-Joumaa in 2009 [91] evaluating the influence of petroleum hydrocarbons on soil physical and chemical properties, the polluted soil exhibited more bulk and absolute density, lower clay fraction, and calcium carbonate content compared to unpolluted soils. Electrical conductivity (EC) values were higher in the polluted soil, with dominant soluble Ca and SO⁴⁻ ions in the unpolluted soil [91]. Electrochemical systems have been recognized for remediating cyclic and aromatic hydrocarbons in polluted media, including soil. These systems utilize electric current as an electron donor or acceptor for oil spill remediation, with mechanisms such as electro-osmosis, electromigration, and electrophoresis facilitating the transport and mobilization of pollutants. Electrical potential and electromagnetic waves are considered green technologies for effective remediation and the volatilization of low molecular weight hydrocarbons. Wang et al. in 2022 led a study utilizing single-chamber air-cathode microbial fuel cells for pyrene degradation, demonstrating its effectiveness. The adding of pyrene also affected the electrical properties of microbial fuel cells, leading to a rise in the density of the anodic biofilm [85,92].

3. MICROBIAL ELECTROCHEMICAL SYSTEM FOR SOIL BIOREMEDIATION

Soil contamination is a significant hazard to ecosystems and humans. In comparison to traditional physical and chemical treatments, the Microbial Electrochemical System (MES) presents a sustainable and clean solution for soil bioremediation. Essentially, soil microbes break down organic substrates and release electrons in the anode region. These electrons travel through an electric circuit to the cathode, where they are ultimately accepted by oxygen or oxidized metals. MES, with its various inherent advantages, has found application in the bioremediation of petroleum hydrocarbons, chlorinated organics, and heavy metals in soils [9]. Bioremediation involves employing microorganisms, primarily bacteria, to break down hazardous contaminants, convert them into less harmful forms, and/or immobilize them under appropriate environmental conditions [93]. The effectiveness of bioremediation relies on the simultaneous presence of microorganisms, contaminants (which serve as food for the microorganisms), electron acceptors, and essential nutrients for the microbial growth. In fine-grained soils with low hydraulic conductivity, supplying microorganisms, necessary electron

acceptors, or nutrients to contaminants, or providing contaminants to naturally occurring microorganisms, can be challenging.

Electrokinetics-enhanced bioremediation, also known as bioelectrokinetics, is a technology that integrates bioremediation with electrochemical remediation. This process involves delivering microorganisms, electron acceptors, or nutrients to contaminants or moving contaminants to microorganisms through electrokinetic flow processes. A notable advantage of electrokinetics-enhanced bioremediation for in situ remediation is its ability to selectively transport bacteria from injection points into zones of contamination [94]. Successful applications of electroosmosis and/or electrophoresis include injecting a Pseudomonas strain (a bacterial cell capable of degrading diesel) into diesel-contaminated soil [95], introducing *Sphingomonas* sp. L138 and *Mycobacterium frederiksbergense* LB501TG (bacteria that degrade polycyclic aromatic hydrocarbons) into laboratory model aquifers made of glass beads, alluvial sand from Lake Geneva, and historically polluted clayey soil [96], and using *Pseudomonas putida, Bacillus subtilis*, and *Klebsiella pneumoniae* to induce bacterial cell migration and facilitate the biodegradation of crude oil in soil [97].

The Microbial Electrochemical System (MES) represents an emerging technique in the realm of bioremediation, seamlessly integrating microbial and electrochemical processes to extract reducing equivalents from organic matter and convert chemical energy into electrical energy [98]. This approach employs a series of redox reactions facilitated by microbial metabolism, leading to the reduction or oxidation of contaminants and the subsequent production of less-toxic or value-added products. Despite variations in electrochemical characteristics across soils, numerous studies have affirmed the viability of utilizing MES for in situ soil bioremediation.

Six distinct mechanisms of MES for soil bioremediation are: (1) Oxidation in the Anode: In this mechanism, contaminants like petroleum hydrocarbons are degraded, serving as electron donors in the anode [98]. (2) Reduction in the Anode: Contaminants accept electrons under reductive conditions in the anode, contributing to the remediation process [99]. (3) Sorption: This involves the adsorption of contaminants from the soil onto electrodes or the biofilm colonized on electrodes, enhancing remediation efficacy [100]. (4) Electrokinetic Processes: An applied electric field induces changes in the physicochemical and hydrologic properties of the soil, influencing the chemical speciation and distribution of contaminants [101] (5) Cathodic Alkalization: As protons are consumed in cathodic oxygen reduction, pH increases in this mechanism, contributing to the overall remediation process [102] (6) Reduction in the Cathode: This mechanism involves halogenated organics, nitroaromatics, azo dyes, and highvalent metals obtaining electrons generated from the anode, leading to their reduction and subsequent remediation [101,103,104]. These multifaceted mechanisms underscore the versatility and potential effectiveness of MES in addressing various contaminants through intricate interplays of microbial and electrochemical processes [105].

In a 2016 study, a novel approach was introduced, combining electrokinetics with microbial degradation to effectively break down cycloparaffinic hydrocarbons in soil. Cyclododecane, serving as a model pollutant, was introduced into soils at a concentration of approximately 1000 mg kg⁻¹. A mixture of petroleum-utilizing bacteria, achieving a count of about 10⁶-10⁷ CFU g⁻¹, was subsequently introduced. The study involved three distinct treatments conducted over a period of 25 days: (1) no electric field (control); (2) a constant voltage gradient of 1.3 V cm⁻¹ in one direction; and (3) the same electric field with periodic switching of polarity.

Although the degradation pathway of cyclododecane remained unchanged with the electric field, dynamic processes were significantly enhanced, particularly during the periods of periodic polarity switching. At the end of the 25-day period, the degradation rates were notably higher in tests 2 and 3, with 79.9% and 87.0% of cyclododecane degraded, respectively, compared to the 61.5% degradation observed in test 1. Analysis of intermediate products suggested that the electric field's competitive advantage lay in increased ring-breaking of cyclododecane, leading to higher concentrations of linear substances that were more susceptible to microbial attack, specifically through β -oxidation processes. Conditions near the cathode favored microorganism growth and metabolism, further enhancing β-oxidation of linear alkanoic acids. Periodic electrode polarity switching applied the functions of both anode and cathode electrodes across the entire soil cell, amplifying degradation efficiency. This study provides a comprehensive exploration of electrobiodegradation mechanisms leading to the breakdown of cycloparaffinic hydrocarbons in soil. The electric field increased ring-breaking in the anode region and enhanced β -oxidation near the cathode. Additionally, amending Bacillus and Arthrobacter species into soils before electrokinetic remediation could further improve total petroleum hydrocarbon degradation [106].

4. PHYTOREMEDIATION -ELECTROCHEMICAL HYBRID

Phytoremediation encompasses a series of processes that utilize plants to either eliminate environmental pollutants or render them harmless. Critical steps in phytoremediation, such as phytoextraction, phytostabilization, and rhizodegradation, involve plant uptake, translocation, and accumulation of contaminants [107]. The presence of plants contributes to contaminant degradation through root enzymes [108]. Various factors, including the addition of fertilizer, soil salinity balance, pH, and nutrients, influence the efficiency of phytoremediation (phytoR). Electroremediation (ER) is an in-situ method that employs low direct electric current between electrodes embedded in contaminated soils to create an electric field [109,110]. ER utilizes mechanisms such as electrolysis, electro-osmosis, electro-migration, and electrophoresis to facilitate the transportation of pollutants across the soil [111,112]. While phytoR and ER

individually prove efficient in removing organic pollutants, their combined use enhances mass transport [31,113,114]. Applying an electric field near growing plants can boost their remediation capacity by mobilizing nutrients and contaminants for plant uptake [115]. Studies, such as Lemstrom et al. [116] have demonstrated that plants exposed to alternating current (AC) in an electric field exhibit increased growth and biomass production. Another study [117] showed the influence of a constant AC electric field in phytoR, facilitating the transport of metals towards the cathode reservoir and accumulating on the cathode side due to ryegrass's metal accumulation. However, few studies have explored the integration of ER with phytoR for treating soils contaminated with organic pollutants. The innovative approach of combining plant-based remediation with an electric field, applied through the medium, controls the transport of charged and/or non-charged contaminants in the soil within the rhizosphere, preventing strong acidic or alkaline fronts [28]. For instance, a study investigated the synergistic enhancement of phytoremediation (phytoR) efficiency through electrokinetic remediation (ER) using graphite electrodes to decontaminate petroleum-contaminated soil. The research focused on the impact of electric fields, specifically direct current (DC) with reversal polarity (RP), and assessed the growth of sunflower plants post-remediation. Experimental setups included phytoR, ER, and electro-phytoremediation (ER-PhytoR) with DC (ER-PhytoR-DC) or RP (ER-PhytoR-RP). The most effective total petroleum hydrocarbon (TPH) removal occurred with ER-PhytoR-RP at 1 V cm⁻¹ after 20 days. Operational parameters contributing to this efficiency included microbial degradation in the rhizosphere and the transport of organic compounds through the soil associated with RP, preventing acidity and alkaline fronts. RP application significantly promoted plant germination, growth, and high TPH removal after 20 days. The findings showed improved biomass yield across various treatments, with quantities of 5.22 g observed for phytoR, 1.137 g for ER-PhytoR-DC, and 5.89 g for phytoR-ER. Additionally, two diamond-based electrochemical technologies, anodic oxidation (AO-H2O2) and electro-Fenton (EF), effectively treated effluents generated during soil decontamination, eliminating dissolved organic matter [118].

5. CONCLUSION

This review explores recent advancements in electrochemical treatment technology aimed at remediating contaminated soil, addressing the global concern of soil degradation. Given the pivotal role of soil in sustaining human life and fostering sustainable development, the remediation of soil with characteristics such as fine grains, low hydraulic permeability, heterogeneous conditions, and mixtures of contaminants remains challenging for conventional technologies. Electrochemical remediation (ER) technology stands out as an attractive strategy for soil remediation due to its cost-effectiveness, adaptability, and effectiveness as a noninvasive, in situ approach. The method involves applying a direct-current electric field to contaminated soil, utilizing mechanisms like electroosmosis, electromigration, and/or electrophoresis to extract contaminants. This paper provides a comprehensive review of these techniques, aiming to offer valuable insights to researchers and practitioners in the field.

Declarations of interest

The authors declare no conflict of interest in this reported work.

REFERENCES

- [1] S. Dehghan Abkenar, N. Khakipour, and M.R. Ganjali, Pollution 9 (2023) 1538.
- [2] H.C.J. Godfray, J.R. Beddington, I.R. Crute, L. Haddad, D. Lawrence, J.F. Muir, J. Pretty, S. Robinson, S.M. Thomas, and C. Toulmin, Food Security: The Challenge of Feeding 9 Billion People, Science (2010).
- [3] A. Koch, N. Kumar, L. Weber, H. Keller, J. Imani, and K.H. Kogel, Proc. Natl. Acad. Sci. 110 (2013) 19324.
- [4] A. McBratney, D.J. Field, and A. Koch, Geoderma 213 (2014) 203.
- [5] K.C. Seto, M. Fragkias, B. Güneralp, and M.K. Reilly, PLoS One 6 (2011).
- [6] T. Shah, J. Burke, K. Villholth, M. Angelica, E. Custodio, F. Daibes, J. Hoogesteger, M. Giordano, J. Girman, J. van der Gun, E. Kendy, J. Kijne, R. Llamas, M. Masiyandama, J. Margat, L. Marin, J. Peck, S. Rozelle, B. Sharma, L. Vincent, and J. Wang, Groundwater: A global assessment of scale and significance, in: Water for Food Water for Life: A Comprehensive Assessment of Water Management in Agriculture (2013).
- [7] [Onlinle] available at: https://www.fao.org/3/y4502e/y4502e00.htm (2003).
- [8] A.R. Giuliano, and S. Gapstur, Nutr. Rev. 56 (1998) 9.
- [9] A.D.O. Lima, N. da S. Dias, F.P. Lima Filho, M.F. Neto, P.R. do A. Rego, and A. de M. Souza, Rev. Bras. de Eng. Agricola e Ambient 21 (2017).
- [10] H. Li, F. Muhammad, Y. Yan, M. Zhang, B. Jiao, L. Yu, and D. Li, R. Soc. Open Sci. 5 (2018) 180372.
- [11] X. Han, J. Wang, W. Cai, X. Xu, and M. Sun, Int. J. Environ. Res. Public Health 18 (2021) 11243.
- [12] A.T. Yeung, Remediation Technologies for Contaminated Sites, in: Advances in Environmental Geotechnics (2010).
- [13] A.T. Yeung, and Y.Y. Gu, J. Hazard. Mater. 195 (2011) 11.
- [14] J.K. Mitchell, and K. Soga, Fundamentals of soil behavior, John Wiley & Sons New York (2005).
- [15] C.K. Yeung, B. Sreedhar, J.D.Y. Sihoe, F.K.Y. Sit, and J. Lau, B.J.U. Int. 97 (2006) 1069.

- [16] A.T. Yeung, Geochemical Processes Affecting Electrochemical Remediation, in: Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater (2009).
- [17] H. Lin, Z. Wang, C. Liu, and Y. Dong, Chemosphere 305 (2022) 135315.
- [18] M.R. Islam, P. Sanderson, R. Naidu, T.E. Payne, M.P. Johansen, A.S.M.F. Bari, and M.M. Rahman, J. Hazard. Mater. 421 (2022) 126757.
- [19] M. Hosseini, Z. Vaezi, M.R. Ganjali, F. Faridbod, S.D. Abkenar, and M. Salavati-Niasari, Sens. Lett. 8 (2010) 161.
- [20] M. Hosseini, Z. Vaezi, M.R. Ganjali, F. Faridbod, and S.D. Abkenar, Acta A Mol. Biomol. Spectrosc. 83 (2011) 161.
- [21] L. Hajiaghababaei, A. Sharafi, S. Suzangarzadeh, and F. Faridbod, Anal. Bioanal. Electrochem. 5 (2013) 481.
- [22] L. Hajiaghababaei, A. Badiei, M. Shojaan, M.R. Ganjali, G.M. Ziarani, and P. Zarabadi-Poor, Int. J. Environ. Anal. Chem. 92 (2012) 1352.
- [23] Y. Wang, A. Li, and C. Cui, Chemosphere 265 (2021) 129071.
- [24] D.C. Adriano, Trace Elements in the Terrestrial Environment. (1986). https://doi.org/10.2134/jeq1987.00472425001600010030x.
- [25] S. Fakhri, F. Abbaszadeh, L. Dargahi, and M. Jorjani, Pharmacol. Res. 136 (2018) 1.
- [26] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, and R. Parker, J. Hazard. Mater. 40 (1995) 117.
- [27] Y.B. Acar, and A.N. Alshawabkeh, Environ. Sci. Technol. 27 (1993) 2638.
- [28] A. Figueroa, C. Cameselle, S. Gouveia, and H.K. Hansen, J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 51 (2016) 691.
- [29] L.M. Ottosen, K. Lepkova, and M. Kubal, J. Hazard. Mater. 137 (2006) 113.
- [30] C. Cameselle, R.A. Chirakkara, and K.R. Reddy, Chemosphere 93 (2013) 626.
- [31] F.S. Meng, L.Y. Nie, H. Xue, and D.P. Zhang, J. Agro-Environ. Sci. 37 (2018) 1125.
- [32] S. Wang, B. Gao, W. Jiang, D. Huang, W. Ma, S. Liu, and B. Zhang, J. Radioanal. Nucl. Chem. 332 (2023) 843.
- [33] S.D. Abkenar, M. Hosseini, Z. Dahaghin, M. Salavati-Niasari, and M.R. Jamali, Bull. Korean Chem. Soc. 31 (2010) 2813.
- [34] Y. Zheng, H. Li, Q. Yu, L. Yu, B. Jiao, D. Li, J. Hazard. Mater. 416 (2021) 125806.
- [35] Z. Zhu, H. Liu, Y. Yang, X. Zhou, Sh. Tang, L. Zhang, Y. Zhu, and Y Fan, Environ. Technol. Innov. 33 (2024) 103483.
- [36] R. Han, Q. Yu, Y. Zheng, H. Li, Y. Shi, X. Lin, and D. Li, Sep. Purif. Technol. 334 (2024) 126006.
- [37] S. Hu, J. Hu, Y. Sun, Q. Zhu, L. Wu, B. Liu, K. Xiao, S. Liang, J. Yang, and H. Hou, J. Hazard. Mater. 405 (2021) 124072.

- [38] S. Gao, Y. Wang, Z. Wang, X. Tong, and R. Sun, Environ. Sci. Pollut. Res. 29 (2022) 102539.
- [39] H. Chen, Z. Tang, P. Wang, and F.J. Zhao, Environ. Pollution 238 (2018) 482.
- [40] J.N. Hakizimana, B. Gourich, M. Chafi, Y. Stiriba, C. Vial, P. Drogui, and J. Naja, Desalination 404 (2017) 1.
- [41] B.M.B. Ensano, L. Borea, V. Naddeo, V. Belgiorno, M.D.G. de Luna, and F.C. Ballesteros, Removal of pharmaceuticals from wastewater by intermittent electrocoagulation, Water (Switzerland) 9 (2017) 85.
- [42] M. Eyvaz, M. Kirlaroglu, T.S. Aktas, and E. Yuksel, Chem. Eng. J. 153 (2009) 16.
- [43] Y. He, A.E. Bayly, A. Hassanpour, F. Muller, K. Wu, and D. Yang, Powder. Technol. 361 (2020) 473.
- [44] P. Maha Lakshmi, and P. Sivashanmugam, Sep. Purif. Technol. 116 (2013) 378.
- [45] C. Chen, L. Liu, Y. Li, W. Li, L. Zhou, Y. Lan, and Y. Li, Chem. Eng. J. 384 (2020) 123257.
- [46] P. Ju, K.T. Alali, G. Sun, H. Zhang, Q. Liu, J. Liu, J. Yu, R. Chen, and J. Wang, Chemosphere 271 (2021) 129548.
- [47] Q. Zeng, Y. Zhang, P. Chen, Y. He, C. Yi, and C. Feng, J. Environ. Sci. 124 (2023) 89.
- [48] M. Pociecha, and D. Lestan, J. Hazard. Mater. 174 (2010) 670.
- [49] S. Hu, D. Li, C. Huang, D. Sun, and X. Yuan, Sep. Purif. Technol. 189 (2017) 213.
- [50] G.M. Kirkelund, P.E. Jensen, L.M. Ottosen, and K.B. Pedersen, J. Hazard. Mater. 367 (2019) 68.
- [51] M.L. Nyström, G.J. Thomas, M. Stone, I.C. Mackenzie, I.R. Hart, and J.F. Marshall, J. Pathol. 205 (2005) 468.
- [52] L.M. Ottosen, H.K. Hansen, S. Laursen, and A. Villumsen, Environ. Sci. Technol. 31 (1997) 1711.
- [53] L.M. Ottosen, G.M. Kirkelund, and P.E. Jensen, Chemosphere 91 (2013) 963.
- [54] R. Parés Viader, P.E. Jensen, L.M. Ottosen, J. Ahrenfeldt, and H. Hauggaard-Nielsen, Waste Manag. 60 (2017) 211.
- [55] L.M. Ottosen, H.K. Hansen, and C.B. Hansen, J. Appl. Electrochem. 30 (2000) 1199.
- [56] S. Xu, W. Wang, and L. Zhu, Sci. Total Environ. 653 (2019) 1293.
- [57] T. Sun, J. Beiyuan, G. Gielen, X. Mao, Z. Song, S. Xu, Y.S. Ok, J. Rinklebe, D. Liu, D. Hou, J.W.C. Wong, and H. Wang, J. Soils Sediments 20 (2020) 3417.
- [58] Y. Song, L. Cang, Y. Zuo, J. Yang, D. Zhou, T. Duan, and R. Wang, Chemosphere 243 (2020) 125439.
- [59] F. Proietto, A. Khalil, W. Maouch, A. Galia, and O. Scialdone, Environ. Technol. Innov. 32 (2023) 103286.

- [60] F. Proietto, P. Meli, C. Prestigiacomo, A. Galia, and O. Scialdone, J. Environ. Chem. Eng. 12 (2024) 111780.
- [61] S.D. Abkenar, M. Khoobi, R. Tarasi, M. Hosseini, A. Shafiee, and M.R. Ganjali, J. Environ. Eng. 141 (2015) 04014049.
- [62] S. Dehghan Abkenar, M.R. Ganjali, M. Hosseini, and M. Sadeghpour Karimi, Iran. J. Chem. Chem. Eng. 38 (2019) 83.
- [63] L. Hajiaghababaei, S. Abozari, A. Badiei, P. Zarabadi Poor, S. Dehghan Abkenar, M.R. Ganjali, and G. Mohammadi Ziarani, Iran. J. Chem. Chem. Eng. 36 (2017) 97.
- [64] M. Pazos, M.T. Ricart, M.A. Sanromán, and C. Cameselle, Electrochim. Acta. 52 (2007) 3393.
- [65] Q. Liu, Y. Jiang, Y. Liu, X. Zhang, Y. Xu, H. Chen, and W. Cao, Environ. Technol. Innov. 28 (2022) 102835.
- [66] K. Dhar, L. Panneerselvan, K. Venkateswarlu, and M. Megharaj, Biodegradation, 33 (2022) 575.
- [67] P. Makoś, A. Fernandes, and G. Boczkaj, J. Sep. Sci. 41 (2018) 2360.
- [68] H.R. Barzoki, A. Dargahi, A. Shabanloo, A. Ansari, and S. Bairami, J. Water Process. Eng. 56 (2023) 104429.
- [69] M.P. Rayaroth, M. Marchel, and G. Boczkaj, Sci. Total Environ. 857 (2023) 159043.
- [70] G. Boczkaj, and A. Fernandes, Chem. Eng. J. 320 (2017) 608.
- [71] W.F. Elmobarak, B.H. Hameed, F. Almomani, and A.Z. Abdullah, Catalysts 11 (2021) 782.
- [72] S. Srivastav, S. Neupane, S. Bhurtel, N. Katila, S. Maharjan, H. Choi, J.T. Hong, and D.Y. Choi, J. Nutr. Biochem. 69 (2019) 73.
- [73] A.T. Lawal, Cogent. Environ. Sci. 3 (2017) 1339841.
- [74] E. Brillas, J. Clean. Prod. 290 (2021) 125841.
- [75] F. Nemati, M. Hosseini, R. Zare-Dorabei, and M.R. Ganjali, Anal. Methods 10 (2018) 1760.
- [76] C. Rodrigo, D. Fernando, and S. Rajapakse, Crit. Care. 18 (2014) 217.
- [77] M.A. Oturan, and J.J. Aaron, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577.
- [78] M. Malakootian, A. Nasiri, and M. Amiri Gharaghani, Chem. Eng. Commun. 207 (2020) 1.
- [79] C.A. Martínez-Huitle, and M. Panizza, Curr. Opin. Electrochem. 11 (2018) 62.
- [80] P. V. Nidheesh, M. Zhou, and M.A. Oturan, Chemosphere 197 (2018) 210.
- [81] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, and M. Panizza, Environ. Sci. Pollut. Res. 21 (2014) 8336.
- [82] C.A. Martínez-Huitle, and E. Brillas, Appl. Catal. B. 87 (2009) 105.
- [83] S.A. Ganiyu, B.S. Badmus, O.T. Olurin, and Z.O. Ojekunle, Appl. Water Sci. 8 (2018) 35.

- [84] M.B. Carboneras Contreras, F. Fourcade, A. Assadi, A. Amrane, and F.J. Fernandez-Morales, Chemosphere 237 (2019) 124447.
- [85] T.G. Ambaye, A. Chebbi, F. Formicola, S. Prasad, F.H. Gomez, A. Franzetti, and M. Vaccari, Chemosphere 293 (2022) 133572.
- [86] F. Abbasian, R. Lockington, M. Mallavarapu, and R. Naidu, Appl. Biochem. Biotechnol. 176 (2015) 670.
- [87] G.I. Asejeje, A.R. Ipeaiyeda, and P.C. Onianwa, Environ. Sci. Pollut. Res. 28 (2021) 15361.
- [88] P. Mani Acharya, S. Saeung, K. Techato, N. Rimal, S. Gyawali, and D. Neupane, Review of Environmental Policies and Otter Conservation in Nepal (2022).
- [89] P. Logeshwaran, M. Megharaj, S. Chadalavada, M. Bowman, and R. Naidu, Environ. Technol. Innov. 10 (2018) 175.
- [90] T. Steliga, and D. Kluk, Ecotoxicol. Environ. Saf. 194 (2020) 110409.
- [91] H. A.M. Abou-Zeid, A.E. El-Leboudi, M.A. Mostafa, E.M. Abd- Elmoniem, and U.A. El-Behairy, Arab Univ. J. Agri. Sci. 17 (2009) 267.
- [92] H. Wang, P. Chen, S. Zhang, J. Jiang, T. Hua, and F. Li, Sci. Total Environ. 804 (2022) 150153.
- [93] A.C.L. Yeung, J. Oper. Manag. 26 (2008) 651.
- [94] M.F. Deflaun, and C.W. Condee, J. Hazard. Mater. 55 (1997) 263.
- [95] H.S. Lee, and K. Lee, J. Microbiol. Biotechnol. 11 (2001) 772.
- [96] L.Y. Wick, P.A. Mattle, P. Wattiau, and H. Harms, Environ. Sci. Technol. 38 (2004) 4596.
- [97] A. Olszanowski, and K. Piechowiak, Pol. J. Environ. Stud. 15 (2006) 303.
- [98] Z.H. Wang, H.L. Zeng, Y.M. Wei, and Y.X. Zhang, Appl. Energy 97 (2012) 115.
- [99] S. Wang, Q. Yang, F. Chen, J. Sun, K. Luo, F. Yao, X. Wang, D. Wang, X. Li, and G. Zeng, Chem. Eng. J. 328 (2017) 927.
- [100] C. Zhang, H. Zhang, M. Lv, and Z. Hu, J. Non. Cryst. Solids 356 (2010) 1703.
- [101] W. Wang, J. Yu, J. Zou, and X. Yu, Electrochim. Acta 191 (2016) 426.
- [102] Y. Zheng, D.S. Yang, J.M. Kweun, C. Li, K. Tan, F. Kong, C. Liang, Y.J. Chabal, Y.Y. Kim, M. Cho, J.S. Yu, and K. Cho, Nano Energy 30 (2016) 443.
- [103] Y. Wang, P. Zhang, X. Ren, and G. Yi, J. Electrochem. Soc. 158 (2011) A1404.
- [104] Y. Mu, K. Rabaey, R.A. Rozendal, Z. Yuan, and J. Keller, Environ. Sci. Technol. 43 (2009) 5137.
- [105] Y. Wu, X. Jing, C. Gao, Q. Huang, and P. Cai, Chemosphere 211 (2018) 156.
- [106] Y. Yuan, S. Guo, F. Li, B. Wu, X. Yang, and X. Li, J. Hazard. Mater. 320 (2016) 591.
- [107] A.C. Agnello, M. Bagard, E.D. van Hullebusch, G. Esposito, and D. Huguenot, Sci. Total Environ. 563–564 (2016) 563.
- [108] E. Dominguez-Rosado, J. Pichtel, and M. Coughlin, Environ. Eng. Sci. 21 (2004) 2.

- [109] E. Vieira dos Santos, F. Souza, C. Saez, P. Cañizares, M.R.V. Lanza, C.A. Martinez-Huitle, and M.A. Rodrigo, Chemosphere 153 (2016) 205.
- [110] E. Vieira dos Santos, C. Sáez, P. Cañizares, C.A. Martínez-Huitle, and M.A. Rodrigo, J. Hazard. Mater. 322 (2017) 413.
- [111] M. Vocciante, A. Caretta, L. Bua, R. Bagatin, and S. Ferro, Chem. Eng. J. 289 (2016) 123.
- [112] R. López-Vizcaíno, A. Yustres, M.J. León, C. Saez, P. Cañizares, M.A. Rodrigo, and V. Navarro, Electrochim. Acta 225 (2017) 93.
- [113] B.C. Martin, S.J. George, C.A. Price, M.H. Ryan, and M. Tibbett, Sci. Total Environ. 472 (2014) 642.
- [114] F. Rozas, and M. Castellote, J. Environ. Manag. 151 (2015) 153.
- [115] G. Acosta-Santoyo, C. Cameselle, and E. Bustos, Environ. Res. 158 (2017) 118.
- [116] A. Goldsworthy, Electrostimulation of Cells by Weak Electric Currents, in: Electrical Manipulation of Cells (1996).
- [117] C.S. O'Connor, N.W. Lepp, R. Edwards, and G. Sunderland, Environ. Monit. Assess. 84 (2003) 141.
- [118] I.M.V. Rocha, K.N.O. Silva, D.R. Silva, C.A. Martínez-Huitle, and E. V. Santos, Sep. Purif. Technol. 208 (2019) 194.