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Towards Environmental Sustainability: A Comprehensive Review of Electrochemical Methods for Remediating Heavy Metal Contamination in Soil and Water-Achievements, Challenges, and Prospects

Bled Abdalah Fadel Abdala[1], Abduladheim Masoud Mahommed[2]*, Mohammed Abraheem Mohammed Arqeeq[1], Hatem Asteil Ahmed Aljazwei[3], Afya Atoum Baroud[4], Mohamed Omar Abdalla Salem[5]

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[1]*Department of Plant Sciences, Kufra University, Kufra ,Libya*
[2]*Department of Soil & Water, Faculty of Agricultural, Bani Waleed University, Bani Waleed, Libya*
[3]*Higher Institute of Science and Technology Al shatii, Libya*
[4]*Department of Chemistry, Faculty of Science, Bani Waleed University, Bani Waleed, Libya*
[5]*Department of Biology, Faculty of Education, Bani Waleed University, Bani Waleed, Libya*
**Corresponding author:*
abduladheimmasoud@bwu.edu.ly

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A B S T R A C T

Heavy metal contamination of soil and water resources poses severe threats to environmental sustainability and human health. Electrochemical remediation technologies (ERT) have emerged as promising, versatile approaches for treating such contamination. This state-of-the-art review critically examines the fundamental mechanisms underpinning electrokinetic remediation (EKR) for soil and electrochemical treatment (ECT) for water, including electromigration, electroosmosis, electrophoresis, and electrolytic redox reactions at electrodes. We synthesize recent advances in their application for removing common heavy metals (e.g., Pb, Cd, Cr, As, Cu, Zn, Hg). Field-scale demonstrations and hybrid systems (e.g., coupling with permeable reactive barriers, phytoremediation, or chemical enhancement) are highlighted, showcasing enhanced efficiency and broader applicability. Despite significant progress, critical scale-up challenges persist, including energy consumption optimization, managing soil heterogeneity and groundwater flow, electrode stability and cost, secondary waste management, and regulatory acceptance. This review identifies key knowledge gaps and provides targeted recommendations for future research, emphasizing the need for integrated pilot studies, advanced electrode materials, renewable energy integration, standardized performance monitoring protocols, and techno-economic analyses to bridge the gap between laboratory success and widespread field implementation.

نحو استدامة بيئية: استعراض شامل لمعالجة التلوث بالمعادن الثقيلة في التربة والمياه بالطرق الكهروكيميائية – إنجازات وتحديات وآفاق

بلعيد عبدالله فضيل عبدالله [1], عبدالعظيم مسعود محمد [2], محمد ابراهيم محمد ارقيق [1], حاتم اسطيل احمد الجازوي [3] ,عافية التومى بارود[4] ,محمد عمر عبدالله سالم[5]

يشكل التلوث بالمعادن الثقيلة في التربة والموارد المائية تهديدات خطيرة للاستدامة البيئية والصحة البشرية. برزت تقنيات المعالجة الكهروكيميائية (ERT) كمناهج واعدة ومتعددة الاستخدامات لمعالجة هذا التلوث. يستعرض هذا المقال التحليلي الحديث الآليات الأساسية الداعمة للمعالجة الكهروحركية (EKR) للتربة والمعالجة الكهروكيميائية (ECT) للمياه، بما في ذلك :الهجرة الكهربائية،

التناضح الكهربائي، الرحلان الكهربائي، وردود الفعل الأكسدة-الاختزال الإلكتروليتية عند الأقطاب .نقدم أحدث التطورات في تطبيقاتها لإزالة المعادن الثقيلة الشائعة مثل: الرصاصPb ، الكادميومCd ، الكرومCr ، الزرنيخAs ، النحاسCu ، الزنكZn ، الزئبقHg .يُسلط الضوء على التطبيقات الحقلية والنظم الهجينة (مثل: الدمج مع الحواجز التفاعلية النفاذة، المعالجة النباتية، أو التعزيز الكيميائي)، مما يظهر كفاءة محسنة وملاءمة أوسع للتطبيق.رغم التقدم الملحوظ، لا تزال تحديات حرجة قائمة في التوسع النطاقي، تشمل :تحسين استهلاك الطاقة، إدارة عدم تجانس التربة والتدفقات الجوفية، استقرار الأقطاب الكهربائية والتكلفة، إدارة النفايات الثانوية، والقبول التنظيمي .يحدد هذا الاستعراض الفجوات المعرفية الرئيسية ويقدم توصيات محددة للبحث المستقبلي، مؤكداً على الحاجة إلى :دراسات تجريبية متكاملة، مواد أقطاب متقدمة، دمج الطاقة المتجددة، بروتوكولات قياس أداء موحدة، وتحليلات تقنية-اقتصادية لسد الفجوة بين النجاح المعملي والتطبيقات الحقلية واسعة النطاق.

INTRODUCTION

Heavy metal contamination of soil and aquatic environments is a pervasive global environmental crisis, stemming from anthropogenic activities such as mining, industrial discharges, improper waste disposal, agricultural practices (e.g., pesticides, fertilizers), and atmospheric deposition (Chowdhury and Rahman 2024; Pamukcu and Kenneth Wittle 1992; Salem, Abdalah, and Mohamed 2024; Sánchez-Castro et al. 2023). Unlike organic pollutants, metals are non-biodegradable, persist indefinitely, and bioaccumulate through the food chain, posing significant risks to ecosystem integrity and human health, including carcinogenicity, neurotoxicity, and organ damage (Chowdhury and Rahman 2024; Mishra et al. 2018; Salem and moftah Mohamed 2025; Salem and Salem 2023).

Conventional remediation techniques, including excavation and disposal (costly, disruptive), pump-and-treat (inefficient for low permeability, long duration), solidification/stabilization (does not remove contaminants), and chemical washing (generates secondary waste, alters soil properties), often suffer from limitations in effectiveness, cost, sustainability, or applicability to diverse site conditions (Arora and Khosla 2022; Mohammed 2021; Ntsomboh-Ntsefong, Mbi, and Seyum 2024).

Electrochemical remediation technologies (ERT) offer a compelling alternative, leveraging the application of direct electric current to induce contaminant transport and transformation within porous media. Primarily, Electrokinetic Remediation (EKR) targets contaminated soils, sediments, and sludges, while Electrochemical Treatment (ECT) is more commonly applied to contaminated groundwater, wastewater, and leachates. ERT presents distinct advantages: in-situ applicability minimizing disturbance, effectiveness across a wide range of soil permeabilities (including clays), potential for targeted removal or immobilization, and compatibility with various contaminants, particularly ionic species like heavy metals (Li et al. 2023; Rozas and Castellote 2012; Smarzewska and Guziejewski 2021; Zheng, Cui, and Li 2022)

This state-of-the-art review aims to comprehensively analyze the current scientific understanding and technological progress in electrochemical methods for heavy metal remediation in soil and water matrices. It will delve into the fundamental physicochemical mechanisms driving contaminant removal, critically evaluate recent applications and performance through case studies and research findings, and explicitly focus on the significant challenges hindering the large-scale deployment and commercialization of these promising technologies. By synthesizing current knowledge and identifying critical research needs, this review seeks to inform future advancements and facilitate the transition of ERT from bench-scale success to effective field-scale solutions.

Fundamental Mechanisms of Electrochemical Remediation

The efficacy of ERT stems from multiple coupled phenomena initiated upon applying a direct current (DC) electric field between electrodes emplaced within the contaminated medium.

- Electromigration (EM): This is the dominant transport mechanism for ionic species, including free metal cations (e.g., Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}) and oxyanionic metals/metalloids (e.g., CrO_4^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}). Charged ions migrate towards the electrode of opposite charge (cations to cathode, anions to anode) under the influence of the electric field (Acar and Alshawabkeh 1993; Virkutyte, Sillanpää, and Latostenmaa 2002). EM is highly efficient for soluble ionic contaminants.

- Electroosmosis (EO): The electric field induces a net flow of pore water from the anode towards the cathode. This occurs due to the interaction between the electric field and the excess charge (usually negative) on soil particle surfaces, creating a mobile diffuse double layer (Pamukcu and Kenneth Wittle 1992; Yeung 2011). EO is crucial for transporting dissolved contaminants (including metals complexed with dissolved organic matter) and for enhancing reagent delivery (e.g., conditioning fluids) in low-permeability soils. The direction can reverse in some low-pH environments.

• Electrophoresis (EP): Negligible in most soil remediation contexts, EP involves the movement of charged colloidal particles or micelles relative to the suspending fluid under an electric field (Probstein 2005).

Electrolytic Reactions at Electrodes: Critical chemical transformations occur at the electrode-electrolyte interface:

• Anode: Water oxidation generates H^+ ions (acid front) and oxygen gas: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. This lowers the pH near the anode, promoting desorption and dissolution of cationic metals bound to soil surfaces. Some metals can be oxidized (e.g., Cr(III) to more mobile Cr(VI) – often undesirable; As(III) to As(V) – potentially beneficial for adsorption).

• Cathode: Water reduction generates OH^- ions (base front) and hydrogen gas: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. This increases pH near the cathode, leading to precipitation of cationic metals as hydroxides, carbonates, or other insoluble species. Reduction can also occur directly for some metals (e.g., Cr(VI) to Cr(III), which precipitates; U(VI) to U(IV)).

• Geochemical Changes: The generated H^+ and OH^- fronts migrate into the soil, inducing significant pH gradients (typically anode pH 2-4, cathode pH 10-12). These pH changes profoundly affect metal speciation, solubility, sorption/desorption behavior, and mineral dissolution/precipitation throughout the treated zone (Reddy and Chinthamreddy 2004; Sun et al. 2023).

Applications: Soil, Water, and Sludges

• Soil Remediation (EKR): EKR has been extensively studied for metal-contaminated soils. Success depends heavily on metal speciation, soil buffering capacity, and organic matter content.

Common strategies include:

Unenhanced EKR: Primarily relies on EM and EO-induced transport. Effective for highly soluble/ionic metals but often limited by precipitation near the cathode (e.g., $Pb(OH)_2$, $Cu(OH)_2$) hindering further removal (Page and Page 2002). Acidic soils or metals forming soluble anionic complexes (e.g., Cd-chlorides) show better removal.

Conditioning/Enhancement: Critical for improving efficiency. Catholyte conditioning (e.g., with acetic acid, citric acid, EDTA) prevents hydroxide precipitation and solubilizes precipitated metals, allowing their continued migration to the cathode chamber (Puppala et al. 1997). Anolyte conditioning (e.g., with chelants) can aid in desorbing strongly bound metals. Recent focus is on biodegradable, less persistent enhancers (e.g., low-molecular-weight organic acids, humic substances)(Liu et al. 2023; Rozas and Castellote 2012).

Hybrid Systems: Coupling EKR with other technologies enhances performance:

• PRBs (Permeable Reactive Barriers): Installing reactive materials (e.g., zero-valent iron, zeolites, activated carbon) between electrodes to trap/immobilize migrating metals (Ho et al. 1999).

• Phytoremediation: Plants placed near the cathode uptake metals concentrated or mobilized by the electric field (phytoremediation-EK) (Ali, Khan, and Sajad 2013; Ghosh and Singh 2005; Masoud 2017; Mohamed et al. 2025; Tangahu et al. 2011).

• Biological Stimulation: Electric field can enhance microbial activity for bio-reduction or bio-sorption of metals.

Water/Groundwater Remediation (ECT): Techniques focus on electrodes within the aqueous phase:

• Electrocoagulation (EC): Sacrificial metal anodes (typically Fe or Al) dissolve, generating metal cations (Fe^{2+}/Fe^{3+}, Al^{3+}) that hydrolyze to form amorphous hydroxides/oxyhydroxides (Sadaf et al. 2024). These flocs adsorb, entrap, and co-precipitate dissolved heavy metals, removed by sedimentation/filtration. Highly effective for various metals (e.g., As, Cr, Cd, Cu, Ni, Zn) in wastewater.

• Electrodeposition (ED): Direct reduction of metal cations (e.g., Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}) onto the cathode surface, recovering metals in metallic form. Suited for concentrated streams and metal recovery (Fertu, Bulgariu, and Gavrilescu 2024).

• Electrooxidation/Electroreduction: Direct electron transfer at inert electrodes (e.g., Ti/Pt, BDD) to destroy complexes or alter oxidation state (e.g., reducing Cr(VI) to Cr(III) at cathode; oxidizing CN^- complexes) .

• Electrodialysis (EDR): Using ion-exchange membranes to selectively separate ions under an electric field. Cationic and anionic metals can be concentrated into separate streams . Useful for desalination and selective metal removal.

Sludge Treatment:

EKR principles are applied to dewater and simultaneously remove metals from contaminated sludges (e.g., harbor, industrial) by enhancing dewatering

(EO) and mobilizing metals (EM) for collection. EC is also used for sludge conditioning and metal immobilization (Ormeño-Cano and Radjenovic 2024).

Performance and Recent Advances

Recent research demonstrates significant progress:

• Enhanced Removal Efficiencies: Studies report removal efficiencies exceeding 80-95% for target metals like Pb, Cd, Cu, Zn, and As from various soils using optimized conditioning agents (e.g., citrate, EDDS) and operational parameters (current density, duration) (Pamukcu and Kenneth Wittle 1992; Srivastava et al. 2024) . EC consistently achieves >90% removal for multiple metals in water matrices.

• Advanced Electrode Materials: Development focuses on cost-effective, efficient, and stable electrodes. Examples include dimensionally stable anodes (DSAs) like mixed metal oxides (MMO) for ECT, carbon-based materials (graphite felt, carbon nanotubes) for EKR/ECT, and nanostructured electrodes for improved kinetics and selectivity (Acar and Alshawabkeh 1993; Page and Page 2002; Reddy and Chinthamreddy 2004).

• Hybrid System Optimization: Research emphasizes synergistic combinations. Examples include EKR coupled with Fe^0-PRBs for Cr (VI) reduction/immobilization, EK-phytoremediation using hyperaccumulators, and EC integrated with membrane filtration (electrocoagulation-flotation - ECF) (Virkutyte et al. 2002).

• Renewable Energy Integration: Pilot studies explore powering ERT using solar photovoltaic systems to reduce operational costs and carbon footprint, demonstrating feasibility for remote sites (Moghimi Dehkordi et al. 2024).

• Focus on Multi-contaminant and Complex Matrices: Research increasingly addresses remediation of sites co-contaminated with metals and organics (e.g., PAHs, pesticides), requiring tailored electrochemical approaches (Fernández-Marchante et al. 2022; Sánchez-Castro et al. 2023) . Studies also focus on complex industrial wastes and sludges.

Scale-Up Challenges and Limitations

Despite promising lab results, widespread field implementation faces substantial hurdles:

• High Energy Consumption: Long treatment times (weeks to months for soil EKR) and ohmic losses lead to significant electricity costs, a major economic barrier, especially for large or deep contamination. Optimization of voltage/current regimes and renewable integration are critical.

• Soil Heterogeneity and Geochemical Complexity: Variations in soil texture, mineralogy, pH buffering capacity, organic matter, and natural groundwater flow drastically impact contaminant transport, reaction kinetics, and overall process efficiency, making predictability and uniform treatment difficult (Lamma, Mohammed, and Aljazwei 2020; Masoud 2017).

• Electrode Design, Stability, and Cost: Electrode degradation (corrosion, passivation, fouling) is common, especially with high currents or reactive species. The cost of robust, long-lasting electrodes (e.g., MMO, BDD) for large-scale applications remains high. Optimal electrode configuration (spacing, geometry) for complex field sites is challenging.

• Management of Secondary Wastes and By-products: EKR generates acidic and basic process waters enriched with mobilized contaminants, requiring collection and treatment (e.g., precipitation, ion exchange, ED). EC generates metal-laden sludge requiring safe disposal. Gas evolution (H_2, O_2) necessitates venting and safety measures.

• pH Management and Side Reactions: Controlling the extreme pH fronts and their migration is crucial but difficult. Undesirable side reactions include re-precipitation of metals away from collection zones, oxidation of Cr(III) to Cr(VI) at the anode, or generation of chlorine if chlorides are present.

• Regulatory Acceptance and Lack of Standard Protocols: Regulatory frameworks often lag behind technological innovation. Lack of standardized design, performance monitoring, and verification protocols for field-scale ERT hinders regulatory approval and stakeholder confidence.

• Techno-Economic Viability: High capital (electrodes, power supply) and operational (energy, waste management) costs, coupled with uncertainties in long-term performance at scale, make robust techno-economic analysis (TEA) and life cycle assessment (LCA) essential but often lacking for specific site applications.

CONCLUSION AND RECOMMENDATIONS

Electrochemical remediation technologies represent a powerful and versatile suite of tools for addressing the persistent challenge of heavy metal contamination in soil and water. Decades of research have elucidated the complex interplay of electromigration, electroosmosis, electrolytic reactions, and geochemical transformations that drive contaminant removal and transformation. Significant advancements have been made in understanding fundamental mechanisms, optimizing operational parameters (e.g., current density, electrolyte conditioning), developing novel electrode materials, and designing effective hybrid systems (e.g., EKR-PRB, EK-phytoremediation, EC-filtration). Laboratory and pilot-scale studies consistently demonstrate high removal efficiencies (often >80%) for a wide range of heavy metals under controlled conditions.

However, the transition from promising laboratory results to routine, cost-effective field-scale application remains hampered by significant scale-up challenges. These include prohibitive energy consumption, difficulties in managing soil heterogeneity and complex geochemistry, electrode degradation and cost, the generation and treatment of secondary wastes/by-products, challenges in controlling pH gradients and unwanted side reactions, and a lack of standardized protocols and robust regulatory frameworks. The techno-economic viability for large-scale projects is often uncertain.

To overcome these barriers and realize the full potential of electrochemical remediation, the following targeted research and development efforts are critically recommended:

1. Pilot-Scale Integration and Long-Term Monitoring: Prioritize large, integrated pilot-scale demonstrations under real-world conditions (complex geology, groundwater flow). Implement comprehensive, long-term (>1 year) monitoring programs to assess treatment efficacy, stability, secondary impacts, and cost performance, generating essential data for regulators and industry.
2. Advanced Electrode and Material Science: Accelerate R&D into low-cost, highly efficient, corrosion-resistant, and selective electrode materials (e.g., nanostructured carbons, novel MMO formulations, conductive composites). Explore self-cleaning or regenerable electrodes. Develop cost-effective, biodegradable, and target-specific conditioning agents for soil EKR.
3. Energy Efficiency and Renewable Integration: Intensify efforts to optimize energy input strategies (e.g., pulsed current, variable voltage gradients). Develop robust models for energy demand prediction. Expand field demonstrations coupling ERT (especially EKR) directly with renewable energy sources like solar PV, including energy storage solutions for continuous operation.
4. Smart Process Control and Modeling: Develop advanced real-time process control systems utilizing sensors (pH, conductivity, redox potential, contaminant concentration probes) and adaptive algorithms to dynamically adjust operating parameters (current, voltage, electrolyte flow/composition) in response to changing subsurface conditions. Enhance predictive multi-physics models (coupled electrochemical, hydrodynamic, geochemical, thermal) for reliable design and performance forecasting.
5. Sustainable Management of Secondary Streams: Innovate efficient, low-cost, and environmentally sound methods for treating and valorizing process waters (e.g., selective metal recovery via electrodeposition or ion exchange, water recycling) and sludges (e.g., stabilization, resource recovery) generated during ERT.
6. Standardization and Regulatory Engagement: Establish industry-wide standardized protocols for ERT design, implementation, performance monitoring, and verification. Proactively engage with regulatory agencies to develop clear, science-based guidelines and approval pathways for electrochemical remediation technologies. Conduct comprehensive TEAs and LCAs for different ERT configurations and site scenarios.

Addressing these research priorities through collaborative efforts between academia, industry, and regulators is paramount to overcoming the current scale-up bottlenecks. By focusing on efficiency, cost reduction, robustness, and sustainability, electrochemical methods can solidify their position as indispensable tools for restoring heavy metal-contaminated environments globally.

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