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(Review Article)

Electrodialysis and hybrid membrane systems for sustainable removal and recovery of toxic metal ions from water and industrial effluents: A systematic review

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Abstract

The release of toxic metal ions from industrial effluents poses environmental and public health risks because of their non-biodegradability and bioaccumulation potential. Conventional treatment methods such as chemical precipitation, coagulation–flocculation, adsorption, ion exchange, and electrocoagulation often have low selectivity, generate secondary waste, and offer limited options for metal recovery; therefore, efficient, sustainable solutions are needed. Electrodialysis (ED) and hybrid membrane systems have emerged as promising alternatives, providing electrically assisted, selective ion separation that requires fewer chemicals and improved potential for metal recovery. This systematic review critically evaluates recent developments in ED and hybrid membrane technologies for the sustainable removal and recovery of toxic metal ions from water and industrial effluents. Following the PRISMA guidelines, the search for peer-reviewed literature was conducted across Scopus, Web of Science, ScienceDirect, Google Scholar, and PubMed databases, employing standardized Boolean search strategies, filtered for relevance and methodological robustness. Comparison analysis focused on system configuration, membrane material, performance metrics, and sustainability measures. Findings reveal significant progress in ion selectivity, energy efficiency, and recovery efficiency through advanced ion-exchange membranes, electro-deionization, and hybrid-electrodeionization-based systems integrated with adsorption, electrochemical oxidation, and nanofiltration. However, challenges such as membrane fouling, high energy consumption, and limited scalability remain unresolved. ED systems and hybrid membrane systems represent a transformative route for sustainable metal ion recovery. Further innovation in membrane materials, hybrid process integration, and pilot-scale validation is vital to achieving industrial-scale implementation.

Keywords: Electrodialysis; Hybrid membranes; Fouling; Industrial effluents; Electrodeionization

1. Introduction

Contamination of water resources with toxic metal ions such as copper (Cu^{2+}), chromium (Cr^{3+}/Cr(VI)), nickel (Ni^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), and zinc (Zn^{2+}) is one of the most pressing global environmental and public health issues [1]. Rapid industrial growth, urbanization, and improper wastewater management have accumulated these pollutants in aquatic ecosystems, resulting in prolonged ecological damage and increased health risks to humans. These metals, even at very low concentrations, can be toxic, causing neurotoxicity, carcinogenic effects, kidney and liver dysfunction, as well as bioaccumulation in the food chains [2]. Governments and international regulators have responded to the issue by establishing strict discharge limits, especially for effluents from mining, electroplating, battery manufacturing, metal finishing, and other heavy industries [3, 4]. Compliance with these regulations is becoming a challenge for industries, especially when treating complex effluents that contain mixed-metal load and high organic content.

Conventional treatment methods, such as chemical precipitation, coagulation-flocculation, adsorption, and ion exchange, have shown large-scale industrial application and therefore have been widely utilized [5]. However, these

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methods have drawbacks such as the generation of large volumes of chemical sludge and low selectivity in multi-ion environments, which lead to high operational costs and limited recovery of metals [6]. As industries move towards circular economy concepts and sustainable resource management, innovative water treatment technologies that effectively remove metal ions and allow the recovery and reuse of valuable metals are urgently needed.

Electrodialysis (ED) and hybrid membrane systems have emerged as promising solutions to tackle these challenges. ED is an electrically driven separation technology that transports ions across alternating cation- and anion-exchange membranes under an applied electric field, concentrating contaminants into a separate stream while producing a purified effluent [7]. ED, unlike traditional chemical treatment, minimizes chemical input, reduces secondary waste, and enables selective recovery of targeted metal ions. Over the last five years, there have been remarkable advancements in ED membrane materials, such as the development of super-selective cation- and anion-exchange membranes, monovalent-ion-selective membranes, and bipolar membranes that can produce both acid and base concurrently [8, 9]. Different variations of method, such as electrodialysis reversal (EDR) and selective electrodialysis (SED), have enhanced operational stability and fouling resistance, broadening the range of suitable applications to complex industrial effluents [10, 11].

The growing interest in ED and hybrid membrane systems aligns with sustainability requirements, such as water recycling, energy efficiency, and circular resource management. These technologies enable the recovery of metals with a purity often unattainable by conventional methods from wastewater streams, contributing to critical resources supply chains for metals with strategic and industrial importance [12]. Moreover, the use of hybrid ED processes in the industrial sector can be a greener option by reducing chemical consumption, producing less sludge, and requiring less energy compared to separation methods that are purely thermal or chemical. However, optimization of the system's performance for real-world applications remains a challenge. Membrane fouling caused by organic and inorganic matter, scaling, and biofilm formation reduces ion transport efficiency, while high energy demands coupled with insufficient techno-economic analyses limit widespread industrial adoption [13]. The development of fouling-resistant membranes, energy-efficient configurations, and process integration strategies is important. Recent developments in polyvinyl alcohol (PVA)-based hybrid membranes further highlight this potential. For example, PVA incorporated with activated clay and hydroxyapatite is reported to achieve up to 95.5% methylene blue dye removal and a flux recovery rate of 83.9%, showing its excellent antifouling performance [14]. Such results achieved corroborate the significance of hybrid materials in broadening the applicability of membrane-assisted water treatment beyond metals to organic pollutants while simultaneously tackling fouling limitations.

Despite growing literature on electrodialysis and hybrid membrane systems, existing reviews often provide a general overview of membrane technologies and limit the discourse to desalination and water softening applications [15]. There is a lack of systematic analysis specifically examining recent improvements in ED and hybrid systems for the sustainable removal and recovery of toxic metals from industrial effluents [16]. Performance metrics of many studies are reported in isolation without placing them in the context of sustainability, resource recovery, and industrial feasibility [17, 18]. Therefore, a comprehensive and current review that provides a critical evaluation of technological advancements, performance outcomes, limitations, and emerging trends is essential. This review aims to bridge the gap by synthesizing fifty-two (52) published papers from 2020 to 2025, comparing performance on various ED setups, hybrid methods, and membrane materials, and pointing out the unresolved challenges and future research opportunities. This study synthesizes recent evidence and provides a guide for researchers, engineers, and policymakers seeking to apply eco-friendly, efficient techniques for the remediation of toxic metals and recovering resources in water and industrial discharges.

2. Methodology

2.1. Literature Search Strategy

This systematic review was carried out in accordance with the PRISMA 2020 [19] to ensure methodological robustness, transparency, and comprehensive coverage of the available literature. The review protocol was structured to scrutinize global studies on electrodialysis and hybrid membrane systems for the removal and recovery of toxic metal ions from water and industrial effluents, focusing on system performance, membrane materials, operational parameters, hybrid configurations, energy consumption, strategies for mitigating fouling, and sustainability considerations. Fifty-two (52) empirical studies published between 2020 and 2025 on recent technological advances and hybrid system innovations were carefully evaluated. Laboratory-scale experiments, pilot-scale applications, and modelling studies reporting either quantitative or qualitative performance outcomes related to metal ion removal, recovery efficiency, energy requirements, and system stability were included in the eligible studies.

A comprehensive and organized literature search was performed across multiple scientific databases, including Web of Science, PubMed, Scopus, ScienceDirect, and Google Scholar. All databases were subjected to a unified Boolean search strategy with minor adjustments made to accommodate indexing and search syntax differences: ("electrodialysis" OR "electrodeionization" OR "ED" OR "electro-membrane") AND ("toxic metal ions" OR "heavy metals" OR "Cu" OR "Pb" OR "Cr" OR "Ni" OR "Cd" OR "Zn") AND ("industrial wastewater" OR "effluent" OR "industrial effluents" OR "wastewater treatment") AND ("hybrid membrane system" OR "ED hybrid" OR "ED+adsorption" OR "ED+electrochemical" OR "membrane integration") AND ("metal recovery" OR "resource recovery" OR "removal efficiency" OR "selectivity" OR "energy consumption")

2.2. Data Extraction

A framework for structured data extraction was designed to ensure reliable and comprehensive recording of study characteristics. The following variables were investigated for each included article:

- **Bibliographic details:** authors, year of publication, country, and study design (laboratory, pilot, modelling).
- **Effluent properties:** industrial wastewater type, metal ion composition, concentration ranges, pH, and salinity.
- **Target metal ions:** Cu^{2+}, Pb^{2+}, Ni^{2+}, Cr^{3+}/Cr(VI),Cd^{2+}, Zn^{2+} or others as applicable.
- **Membrane and system setup:** type of membranes (cationic, anionic, bipolar, monovalent-selective), hybrid combinations (ED+EDI, ED+adsorption, ED+electrochemical oxidation), cell design, and flow arrangements.
- **Operational parameters:** voltage/current density, flow rates, feed concentrations, temperature, and applied pressure.
- **Performance metrics:** removal efficiency (%), recovery efficiency (%), ion selectivity, energy consumption (kWh/m^3), current efficiency, and system stability over time.
- **Fouling and scaling mitigation strategies:** pre-treatment methods, membrane cleaning protocols, antifouling coatings, and reversal techniques.
- **Sustainability indicators:** chemical consumption, sludge generation, resource recovery potential, circular economy relevance.
- **Limitations and challenges:** technical constraints, scalability issues, reproducibility, and knowledge gaps highlighted by authors.

2.3. Data Synthesis

Extracted data were synthesized systematically and organized by themes to identify trends, breakthroughs, and gaps in the field. A comparative analysis was performed across several domains:

- **Membrane performance:** ion removal and recovery efficiencies, selectivity, fouling resistance, and lifespan.
- **Hybrid system innovations:** ED integration with electro-deionization, adsorption, electrochemical oxidation, nanofiltration, forward osmosis, or membrane distillation.
- **Operational optimization:** influence of voltage, current density, flow rates, feed composition, and pre-treatment strategies.
- **Energy and sustainability assessment:** evaluation of energy consumption, chemical usage, sludge production, and alignment with circular economy principles.
- **Scalability and industrial applicability:** pilot-scale demonstrations, techno-economic considerations, and operational challenges in real effluents.

This structured framework enabled a systematic comparison of study outcomes, identification of methodological drivers of variability, and evaluation of technological readiness. It offered a robust foundation for highlighting prominent trends, unresolved challenges, and potential future research directions for the sustainable elimination and recovery of toxic metal ions using ED and hybrid membrane systems. Figure 1 illustrates the PRISMA Flow diagram showing the article selection process in the study.

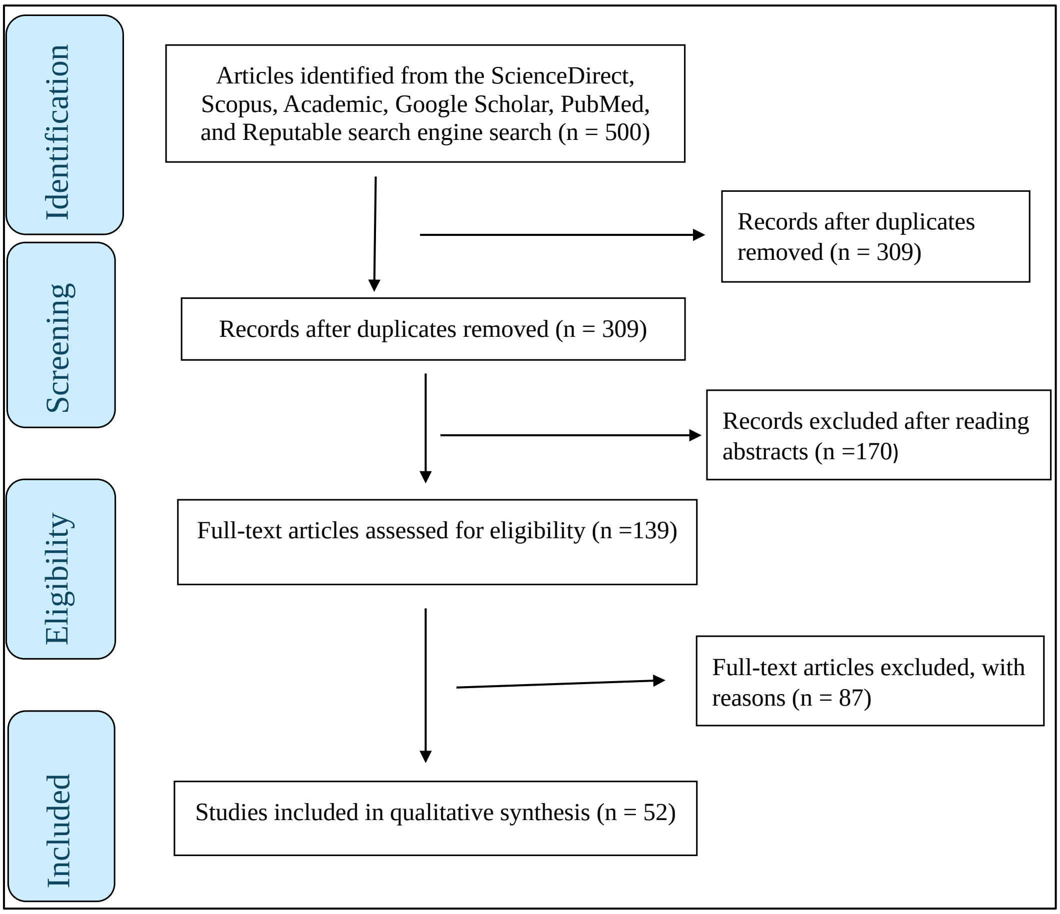

Figure 1 PRISMA Flow diagram showing the article selection process in the study

3. Discussion

3.1. Performance of Conventional Electrodialysis for Toxic Metal Ion Removal

Electrodialysis (ED) (figure 2) is a highly efficient electro-membrane method for the separation of toxic metal ions from water streams, due to its intrinsic selectivity for charged species and its capability to function without extensive chemical additives [20]. ED has been successfully applied to industrial effluents from electroplating, mining, metallurgical processing, battery manufacturing, and tannery operations in a series of studies [21]. These effluents are usually characterized by high ionic strength, mixed-metal compositions, and variable pH, which are conditions where many conventional treatment technologies showed minimal performance. Research studies have shown that ED can remove divalent and multivalent metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} with high efficiency [22]. The separation mechanism is managed by electro-migration through both cation and anion membranes and permits the selective transport of ions according to their charge and hydrated ionic radius. In comparison to chemical precipitation, ED promotes continuous operation and prevents the generation of metal-laden sludge, which poses disposal and secondary pollution challenges [23]. Moreover, ED enables the concentration of metals into a stream, improving downstream recovery.

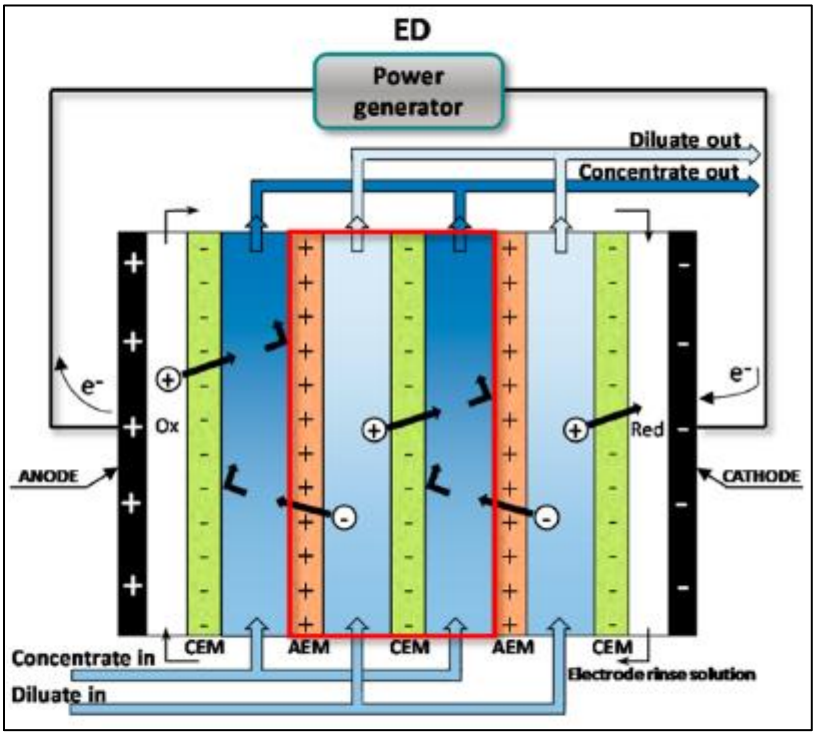

Figure 2 Schematic diagram of conventional electrodialysis [1]

3.2. Advances in Ion-Exchange Membranes and System Configuration

Recent advancements in membrane materials have positively enhanced ED performance in the removal of metal ions. Development of monovalent-selective membranes, surface-modified ion-exchange membranes, and bipolar membranes to enhance selectivity and reduce fouling is reported in various studies [24, 25, 26]. For example, monovalent-selective membranes allow preferential separation of divalent metal ions over monovalent salts, enhancing recovery efficiency in saline industrial effluents [27]. Bipolar membrane electrodialysis (BMED) (figure 3a) has gained much attention for its ability to produce acid and base streams in situ while separating metal ions. This capability is beneficial for acidic mine drainage and metallurgical wastewater treatment, where pH adjustment is vital for metal recovery. By simultaneously controlling pH and ion transport, BMED enhances metal solubility control and reduces external chemical requirements. Electrodialysis reversal (EDR) (figure 3b), a technique that changes the polarity of electrodes at regular intervals, has been demonstrated to mitigate fouling and scaling through the interruption of ion accumulation at membrane surfaces [28]. EDR offers a significant improvement to the operational stability and reduction of cleaning frequency, making it a good option for long-term treatment situations.

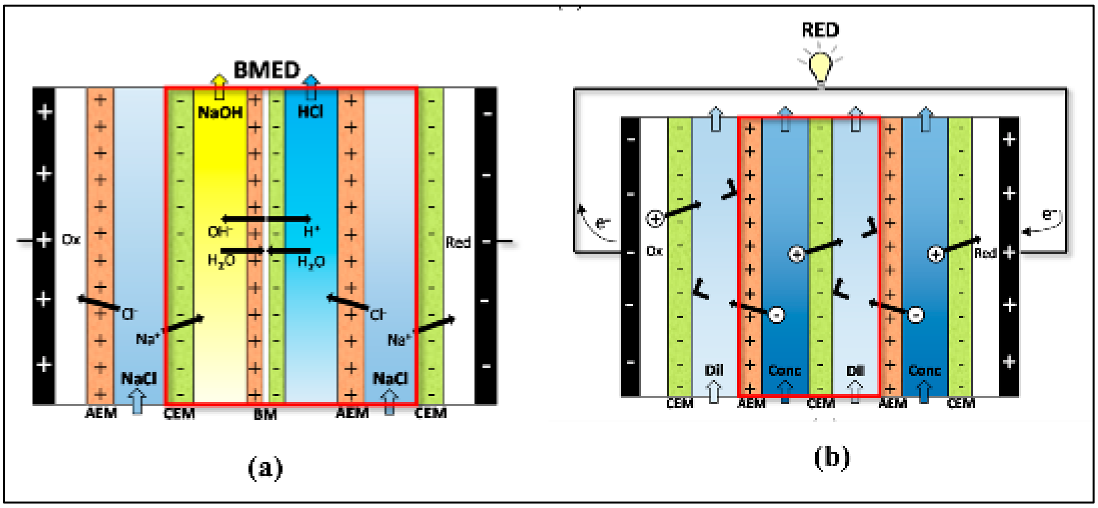

Figure 3 Schematic diagram of (a) bipolar membrane electrodialysis and (b) reverse electrodialysis [1]

3.3. Hybrid Electrodialysis–Membrane Systems: Synergistic Enhancements

The combination of ED with a complementary membrane and electrochemical methods has emerged as one of the major trends in recent research. Hybrid systems are engineered to utilize synergistic mechanisms that improve separation efficiency, reduce energy consumption, and increase system robustness. The use of hybrid material-based techniques has been extensively reported to be effective in various water treatment applications, where the combined action of membrane separation and adsorption results in improved contaminant removal efficiency [29].

3.3.1. ED–Nanofiltration and ED–Reverse Osmosis Hybrids

Nanofiltration (NF) and reverse osmosis (RO) are widely used as pre-treatment or post-treatment methods in hybrid ED systems. NF membranes selectively remove divalent ions and organic matter, thereby reducing the fouling load on the ED membranes [30]. According to studies, NF-ED hybrids achieve high metal recovery efficiencies and lower specific energy consumption compared with a standalone ED system, especially in electroplating and textile wastewater applications [31]. RO-ED systems are effective in concentrating metals from highly saline effluents [32]. In such configurations, RO minimizes total water volume, while ED recovers desired metals from the concentrate stream. This method is especially suitable for the ZLD (zero-liquid-discharge) strategies [33].

3.4. ED Coupled with Adsorptive and Reactive Membranes

Hybrid systems integrating ED with adsorption or reactive membranes represent a conceptual advancement in the selective removal of metal ions. Adsorptive materials such as activated carbon, biochar, metal oxides, and chelating polymers enhance metal capture by surface complexation, while ED enables transport and regeneration of ions [34]. Reactive membranes incorporating nanoparticles, such as iron oxides, manganese oxides, or graphene-based materials, facilitate concurrent processes of electro-migration and chemical binding of metal ions [35, 36]. These systems show high removal efficiencies and improved resistance to fouling, especially in complex wastewaters containing organic contaminants.

3.5. Metal Recovery and Circular Economy Implications

One of the main advantages of ED and hybrid membrane systems is their capacity to recover metals in concentrated and reusable forms. In contrast to adsorption or precipitation processes, ED enables controlled separation and concentration that are suitable for reuse or refining [37]. Recent studies report that when ED is integrated with electro-winning or crystallization units, the recovery of copper, nickel, zinc, and chromium with high purity is achieved [38]. This capacity is particularly relevant in critical metal supply chains and circular economy frameworks, where wastewater is increasingly regarded as a secondary resource rather than a waste stream. Circular economy methods have been investigated in waste management sectors, pointing to opportunities for novel treatment technologies to recover valuable resources from the municipal and industrial waste streams [39]. Table 1 shows a comparison between conventional and hybrid ED Systems in the Removal of Metal Ions

Table 1 Comparison between Conventional and Hybrid ED Systems in the Removal of Metal Ions

System type	Target metals	Reported removal efficiency	Key advantages	Major limitation	References
Conventional ED	Cu^{2+}, Ni^{2+}, Zn^{2+}	85-95%	Low chemical use, selective	Fouling, energy demand	[40, 41]
BMED	Cr, Cu, Ni	90-98%	Acid/base generation, recovery	Higher capital cost	[42, 43]
EDR	Mixed metals	>90%	Reduced scaling, stable operation	Complex control	[44, 45]
Adsorptive ED	Pb^{2+}, Cd^{2+}, Cu^{2+}	96-99%	Enhanced selectivity	Material regeneration	[46, 47]
NF–ED	Pb^{2+}, Cd^{2+}	95-99%	Fouling reduction, selectivity	Multi-unit complexity	[48, 49]

4. Future Directions and Research Gaps

Despite significant progress, critical research gaps remain. First, most research has focused on treating synthetic wastewater matrices, whereas real industrial effluents contain complex mixtures of metals, salts, and organic compounds [50]. Long-term pilot- and full-scale demonstrations are limited, reducing confidence in industrial applicability. Life-cycle and techno-economic assessments are also limited, especially for hybrid systems. Future research should prioritize the fabrication of fouling-resistant membranes, integration with renewable energy sources, and data-driven optimization for intelligent process control. Moreover, developing ED systems capable of selectively recovering critical and rare metals will be important for aligning water treatment with global resource sustainability goals [51, 52].

5. Conclusion

This systematic review highlights electrodialysis and hybrid membrane systems as promising technologies for the sustainable removal and recovery of toxic metal ions from water and industrial effluents. Advances in membrane materials, system configuration, and hybrid integration have enhanced removal efficiency, selectivity, and operational stability compared to conventional treatment methods. Hybrid ED systems showed excellent performance by mitigating fouling, minimizing energy consumption, and allowing high-purity metal recovery. These characteristics set ED-based technologies as essential drivers of circular economy strategies, turning industrial wastewater treatment from a waste management process into a resource recovery platform. Interdisciplinary research, pilot-scale validation, and policy support will be crucial to enabling widespread adoption of these technologies. Electrodialysis and hybrid membrane systems have shown a revolutionary direction for sustainable water treatment and metal resource recovery, with positive effects on environmental protection and industrial sustainability.

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