



Review

Trends in electro-adsorption technologies for rare earth elements recovery: Materials, mechanisms, and future prospects

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ABSTRACT

Electro-adsorption has recently gained significant attention as a sustainable and efficient method for the recovery of rare earth elements (REEs) from low-concentration and chemically complex aqueous environments. Compared with conventional adsorption and electrodeposition techniques, electro-adsorption offers distinct advantages in environmental compatibility, energy efficiency, and ion selectivity. Recent research has focused on the development of highly conductive carbon-based composites, defect-engineered MoS₂ electrodes, and heteroatom-doped frameworks, which exhibit enhanced REE selectivity, rapid charge transfer, and superior cycling stability. The formation and regulation of the electric double layer (EDL) have been identified as the fundamental mechanisms governing adsorption capacity and selectivity. This review systematically summarizes recent developments in electrode material design, adsorption mechanisms (capacitive, redox, and hybrid modes), while evaluating the influence of key operational parameters, such as pH, ionic strength, and applied potential. Furthermore, emerging integration strategies (e.g., coupling with membrane filtration or photoelectrochemical processes) and scale-up approaches using continuous-flow systems are discussed as promising routes toward industrial application. Overall, the insights presented herein not only reveal the evolving design principles of electro-adsorption systems but also outline future directions for achieving efficient, selective, and scalable REE recovery.

1. Introduction

Rare earth elements (REEs), comprising the 15 lanthanides along with scandium and yttrium, are indispensable to a wide range of advanced technologies, such as aerospace systems, permanent magnets, ferrite materials, lasers, and power generation devices [1,2]. Their unique physicochemical properties, particularly strong magnetism and luminescence, underpin their critical role in modern industrial applications. In 2011, global demand for REEs reached approximately 105,000 tonnes ($\pm 15\%$) and has since continued to grow at an annual rate of 5–9% [3]. By 2022, global REE production rose to about 300,000 metric tons of rare earth oxides (REOs), as illustrated in Fig. 1a, which presents country-specific production statistics [4]. China remains both the largest producer and the largest consumer of REEs, with an apparent consumption of approximately 150,000 tonnes of REOs in 2020, followed by Japan, the United States, and the European Union (EU28). Price trends among individual REEs exhibit significant variability (Fig. 1b). Strong demand has driven price increases for elements such as Pr, Nd, Tb, and Dy, whereas elements such as La and Ce have

experienced relatively stable or declining prices due to their greater availability and lower market pressure.

REEs are typically hosted within various mineral matrices, including silicates, carbonates, and phosphates, and are traditionally extracted via mining and mineral processing. Hydrometallurgical processes are commonly used to extract REEs from both primary ores and secondary sources through a sequence of leaching, separation, and purification steps, typically involving acidic or alkaline solutions. However, up to 30% may be lost during processing, often ending up in waste streams such as tailings and slags [5]. In light of the increasing demand and the uneven geographical distribution of REEs, increasing attention has been directed toward alternative secondary sources, such as electronic waste, red mud, and incineration ash [6]. Leachates derived from these resources generally exhibit trace concentrations of REEs, typically ranging from ppb to ppm levels [7]. Despite such extreme dilution, the efficient recovery of REEs from these streams is strategically vital, as traditional separation methods often lack the required sensitivity and selectivity for these ultra-low concentration environments.

A range of methods have been developed for REE recovery,

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predominantly including chemical precipitation, membrane filtration, solvent extraction, and adsorption [8]. Each of these techniques, however, presents inherent limitations. Chemical precipitation often leads to the co-precipitation of impurities (e.g., Fe, Al) and generates large volumes of secondary sludge, increasing operational costs and secondary pollution concerns [9]. Membrane filtration offers effective separation but is constrained by high energy consumption, membrane fouling, and limited-service life. Solvent extraction, although capable of achieving high purity, relies on toxic organic solvents, requires complex process control, and imposes significant environmental burdens. Adsorption-based approaches have attracted considerable attention for REE recovery, and numerous adsorbents have been investigated (Fig. 1d), including activated carbon [10], cellulose [11], silica [12], and titanium dioxide [13]. While these materials demonstrate potential, most do not yet meet the stringent demands for efficient REE recovery from complex, low-concentration aqueous solutions derived from secondary sources. Ideal adsorbents should exhibit high selectivity and adsorption capacity for REEs, chemical stability under harsh conditions (e.g., acidic environments and high salinity), cost-effectiveness, and long-term reusability. In electro-based systems, the stability of the electrode refers to its ability to maintain structural integrity, adsorption performance, and electrochemical activity over repeated adsorption-desorption cycles and prolonged exposure to harsh operating conditions. These material property requirements become particularly critical when dealing with complex leachates from sources such as electronic waste, red mud, incineration ash, and coal-based materials, where REE concentrations are extremely low.

To address these demands, electro-adsorption represents a green and energy-efficient alternative for REE recovery, operating under mild conditions without the use of chemical reagents. This approach enables selective recovery of REEs from dilute and chemically complex matrices while allowing electrode materials to be regenerated and reused [14].

Moreover, electro-adsorption can be coupled with renewable energy sources and integrated with other electrochemical processes, offering promising pathways toward sustainable and circular resource recovery systems. Under an applied electric field, cations and anions are selectively driven toward oppositely charged electrodes, enabling efficient ion separation and concentration. Previous studies have shown that electro-adsorption can be highly effective for extracting trace REEs from dilute aqueous solutions [15]. Beyond REEs, electro-adsorption has also been widely explored for the recovery of other metal ions such as Cu^{2+} , Ag^+ , Pb^{2+} , Hg^{2+} , Ni^{2+} , where it has shown excellent selectivity and cycling stability. As these metals often co-occur in natural and waste-derived aqueous systems, growing interest has emerged in exploring electro-adsorption as a multi-metal ion recovery technique. Electro-adsorption has also been explored for the recovery of lithium, a critical element for energy storage technologies, with encouraging results [16]. In parallel, toxic heavy metals such as mercury, lead, and arsenic, which pose significant environmental and health risks, have also been extensively studied in electro-adsorption systems [17]. While mercury removal has traditionally relied on electrochemical alloy formation on platinum electrodes, recent studies have explored the potential of using electro-adsorption for its removal from contaminated water [18]. Collectively, these studies not only confirm the broad applicability of electro-adsorption principles but also provide valuable insights into electrode surface chemistry, redox-assisted adsorption mechanisms, and structure-property relationships that can inspire the design of improved REE-specific electro-adsorption systems. Despite its considerable promise, to the best of our knowledge, no comprehensive review has yet systematically examined the feasibility, underlying mechanisms, and future prospects of electro-adsorption for REE recovery.

In this review, we begin by outlining the major sources of REEs, with particular emphasis on those present in complex aqueous matrices derived from both primary ores and secondary waste streams, to

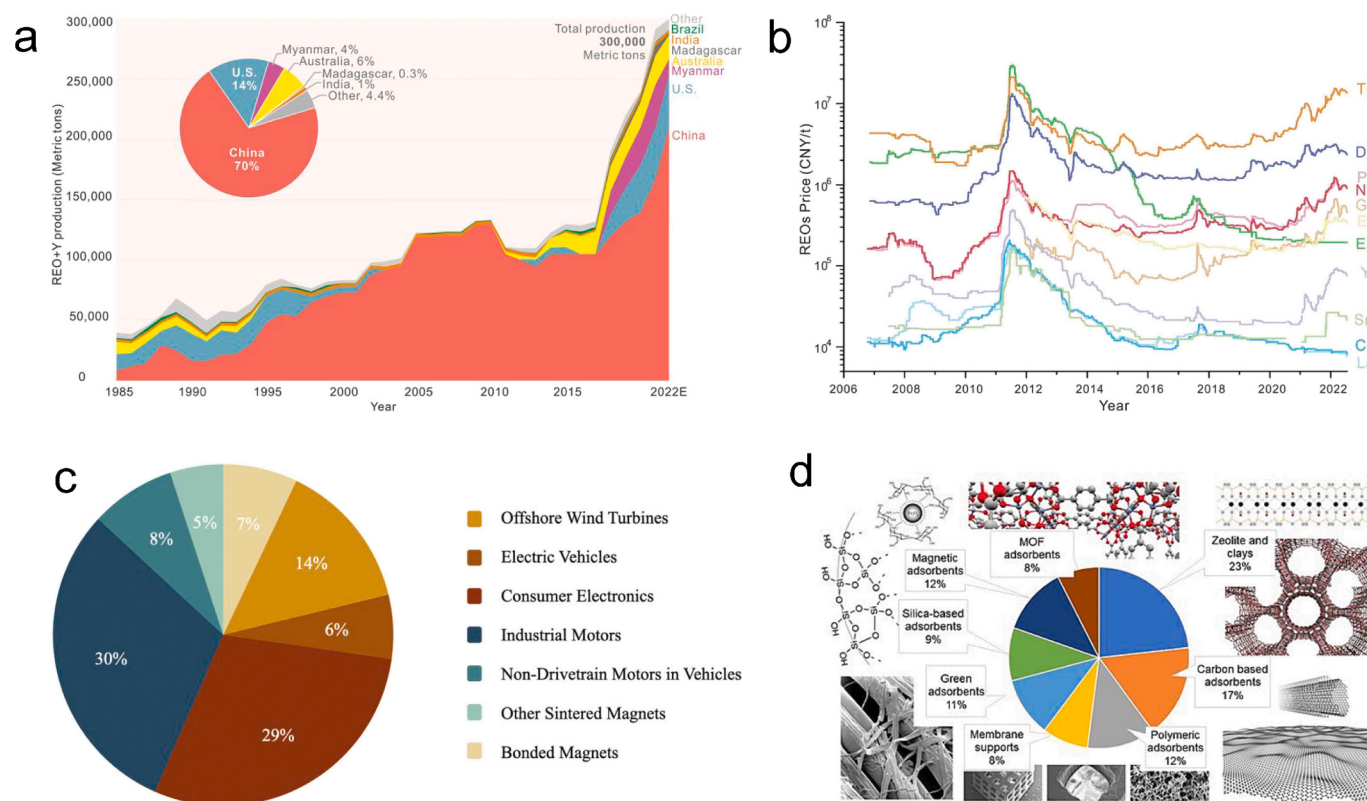


Fig. 1. (a) Global mine production of REO (1985–2022). The insert picture is the production percentage by country in 2022 [4]. (b) Shanghai Metals Market prices of REOs: 2006–2022 (From Wind: <https://www.wind.com.cn/>); (c) demand for Nd-Fe-B magnets, US Department of Energy (2022) [19]; (d) examples of functional materials developed for REE recovery [8].

establish a foundation for evaluating their recovery potential. We then introduce key theoretical concepts underpinning electro-adsorption, particularly the electric double layer (EDL) theory, which governs ion migration and selectivity at the electrode-solution interface. Next, we comprehensively examine advances in electrode material design, interfacial interactions, and the optimization of key operational parameters that influence electro-adsorption performance. Finally, we highlight the key challenges and emerging opportunities associated with electro-adsorption as a sustainable approach for selective REE recovery. Overall, this review aims to fill the existing knowledge gap by synthesizing recent advances, identifying current challenges, and outlining future research directions in this rapidly evolving field.

2. Characteristics of REEs in aqueous systems

Understanding the physicochemical characteristics of REEs in aqueous systems is fundamental to the rational design of electro-adsorption processes. Factors such as competing ion species, solution pH, and ionic strength directly influence EDL formation and ion migration at the electrode-solution interface.

2.1. Compositional complexity of primary and secondary leachates

REE are primarily mobilized into aqueous phases through hydro-metallurgical leaching [20] of primary ores (e.g., monazite, bastnaesite) [21] or secondary waste materials (e.g., spent magnets, fly ash). The surging global demand for NdFeB-based permanent magnets, as illustrated in Fig. 1c, underscores the strategic importance of recovering REEs from these spent magnetic materials [22]. These leachates are typically characterized by a high degree of chemical heterogeneity, which poses significant challenges for selective REE recovery.

In leachates derived from primary mineral resources, REEs commonly coexist with high concentrations of impurity cations such as Al^{3+} , Fe^{3+} , Ca^{2+} , and Mg^{2+} . For instance, in ion-adsorption clay leaching, ammonium-based lixiviants result in solutions dominated by NH_4^+ . The concentration ratios of these competing impurity ions to REEs can range from 10:1 to greater than 100:1, necessitating electrode materials with high selectivity to enable effective electro-adsorption [23].

The aqueous chemistry of REE leachates is also strongly influenced by the choice of lixiviant, with SO_4^{2-} , Cl^- , or NO_3^- often constituting the dominant background anions. Acid mine drainage (AMD) refers to the highly acidic, metal-rich wastewater generated when sulfide-bearing minerals in mines are exposed to oxygen and water. Recently, AMD has been recognized as a significant secondary resource for REEs, where REEs primarily exist as sulfate complexes (REE-SO_4^+) [24], whereas chloride-dominated backgrounds are more common in leachates generated from spent magnet processing [25]. Beyond these mineral acid systems, organic acids (e.g., citric, malic, and succinic acids) have also been explored as sustainable leaching reagents for REEs from coal refuse and other secondary resources [91]. These organic ligands can form stable chelation complexes with REEs, which significantly alter their speciation and increase their effective hydrated ionic radii. Such modifications in the ionic environment, either driven by mineral or organic species, fundamentally dictate the electro-adsorption kinetics, steric hindrance effects, and competitive selectivity at the electrode interface.

Leachates derived from secondary sources like spent NiMH batteries or fluorescent phosphors are often strongly acidic ($\text{pH} < 2.0$) [26], where competition from protons (H^+) represent a dominant inhibitory factor for electro-adsorption. In contrast, certain industrial effluents may reach near-neutral conditions, leading to the risk of premature REE hydrolysis and precipitation, which can also complicate recovery processes [27].

2.2. Challenges in selective separation from complex solutions

As summarized in Table 1, REE concentrations in various aqueous systems vary dramatically, from trace levels in natural waters to several thousand mg/L in industrial leaching solutions. However, the core challenge of electro-adsorption lies not only in the low concentration of target ions but more importantly in the compositional complexity of the solutions. In systems such as AMD or mineral leachates, REEs coexist with high concentrations of competing cations (e.g., Al^{3+} , Fe^{3+} , Ca^{2+}) and complex anionic backgrounds (e.g., SO_4^{2-} , Cl^-). By leveraging differences in ionic charge density and hydration energy, electro-adsorption provides a tunable platform capable of discriminating REEs from high-concentration background ions, offering a more sustainable pathway for selective recovery from heterogeneous waste streams.

Understanding the physicochemical characteristics of REE aqueous systems, such as competing ion species, variable pH, and organic/inorganic contaminants, is fundamental to the rational design of efficient electro-adsorption processes. These factors directly influence EDL formation and ion migration behavior at the electrode-solution interface. Therefore, before addressing practical implementation of electro-adsorption for REE recovery, it is essential to establish a clear understanding of the underlying theoretical foundations and mechanistic principles, which are discussed in the following section.

3. Fundamentals and mechanisms of electro-adsorption

3.1. Theoretical foundations of electro-adsorption

Building upon the understanding of REE-bearing aqueous systems described in the previous section, electro-adsorption mechanism can be interpreted through fundamental electrochemical principles. A classical electrochemical system consists of a positive electrode, a negative electrode, and an electrolyte medium [44]. The development of electro-adsorption is deeply rooted in the interplay between porous electrode materials and EDL theory. As early as 1893, Paul Leon Hulin [45] pioneered the integration of electrochemical techniques with porous electrodes, coining the concept of “electrolytic filtration”. Subsequent studies explored hydrogen adsorption on metallic electrodes via galvanostatic transient methods, potential-controlled adsorption of octanol, and the electro-adsorption of neutral organic molecules [46], as depicted in Fig. 2. Major theoretical milestones include Helmholtz's compact double-layer model (1987) [47], the Gouy-Chapman diffuse layer theory (1910–1913) [48,49], Stern's combined model (1924) [50], and Grahame's division of the compact layer into inner and outer Helmholtz planes (IHP/OHP) in 1974 [51]. Together, these contributions form the basis of the widely used Gouy-Chapman-Stern (GSC) model, which describes EDL formation at the interface between a conductive solid and an electrolyte. This framework is particularly applicable under conditions of planar interfaces and non-overlapping EDLs, as typically encountered in nonporous surfaces or large-pore systems.

Table 1
Summary of typical REE concentrations in various sources.

Sources	Typical REE concentrations	Unit	Ref.
Hard coal fly ash	300–500	mg/L	[28,29]
Bottom ash	50–1230	mg/L	[30,31]
Seawater	10–30.6	ng/L	[32]
Groundwater	1–100	ng/L	[33]
Phosphate rock	50–600	mg/L	[34,35]
Acid mine drainage	0.1–10	mg/L	[36,37]
Seawater	10–40	ng/L	[38,39]
Crustal abundance	Averaging ~169.1	mg/kg	[40]
Sm-Co magnets	250–350	g/kg	[41]
NiMH batteries	Averaging ~173	g/kg	[42,43]

(Note: The concentrations of REEs are reported in different units based on the sample type.)

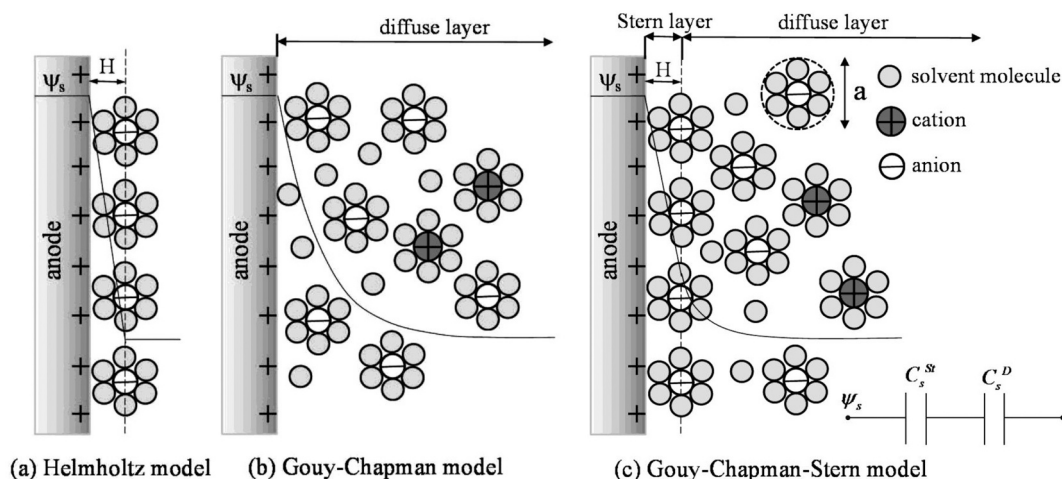


Fig. 2. Schematic illustration of the EDL structure, depicting the distribution of solvated anions and cations at the electrode/electrolyte interface within the Stern layer and the diffuse layer: (a) Helmholtz model; (b) Gouy-Chapman model; and (c) GCS model [52].

Electro-adsorption is a non-Faradaic, heterogeneous interfacial process, wherein species are accumulated on a conductive surface under an externally applied potential or current without net electron transfer [53]. The performance of electro-adsorption is often quantified by the equilibrium electro-adsorption capacity (q_A), reflecting the amount of adsorbate retained per unit mass of electrode material, calculated as [54]:

$$q_A = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate, mg/L; V is the solution volume, L; and m is the mass of the working electrode material, g.

A higher q_A reflects better electro-adsorption efficiency [55]. In this context, the applied electric potential or current serves as an additional driving force beyond mass transport and ionic interactions [56]. Mass transport phenomena, namely diffusion, electromigration, and convection, are critical in electrochemical systems and can be generally described using the Nernst-Planck equation [57]. Under low applied potentials, where no redox reactions occur and only pseudocapacitive currents are present, the adsorption equilibria of charged and neutral species are modulated by the interfacial potential difference. At higher potentials, Faradaic reactions are induced, resulting in redox transformations of the adsorbed species, which may enhance or suppress their adsorption behavior. Beyond mass transport, the interfacial behavior at the electrode/electrolyte boundary significantly affects the electro-adsorption process, primarily through modulation of the EDL structure [58]. EDL properties are influenced by electrode material characteristics, inter-electrode spacing, and electrolyte composition.

To further rationalize electro-adsorption, several mechanistic models have been developed to describe the equilibrium and kinetics of ion accumulation at charged interfaces. A common approach is to extend classical adsorption isotherms by incorporating the effect of interfacial potential difference ($\Delta\phi$). For example, the Langmuir-type electro-adsorption model can be expressed as:

$$q = \frac{q_{\max} K \exp\left(-\frac{zF\Delta\phi}{RT}\right) C}{1 + K \exp\left(-\frac{zF\Delta\phi}{RT}\right) C} \quad (2)$$

where q is the adsorption capacity at equilibrium, $q_{\max}$ is the maximum adsorption capacity, K is the intrinsic adsorption equilibrium constant, z is the ionic charge number, F is Faraday's constant, R is the gas constant, T is the temperature, and C is the bulk concentration of the adsorbate.

This formulation highlights how applied potential modifies adsorption affinity beyond classical chemical driving forces.

In addition to the equilibrium models, kinetic descriptions of electro-adsorption often couple surface coverage with ion transport via the Nernst-Planck equation, allowing analysis of both diffusion-limited and potential-controlled regimes. Together, these mechanistic frameworks provide a quantitative foundation for understanding how electrode potential, ionic charge, and electrolyte composition collectively govern electro-adsorption efficiency.

3.2. Influence of electrode material properties on electro-adsorption

Although numerous studies have explored various factors influencing electro-adsorption performance, including applied voltage, pH, ionic strength, conductivity, residence time, and flow rate [59], this section primarily focuses on the fundamental effects of electrode material properties, which provide more generalizable and transferable insights across systems. In contrast, operational parameters such as solution pH are often system-specific and will be discussed later in the context of REE recovery applications. The intrinsic characteristics of electrode materials, particularly their surface structure and electrical properties, govern the interfacial behavior and are therefore essential for understanding electro-adsorption mechanisms at a fundamental level.

3.2.1. Electrode material types and characteristics

The efficiency of electro-adsorption is partly determined by the intrinsic properties of electrode materials, including specific surface area, porosity, electrical conductivity, surface functional groups, and wettability. Electrode materials used in electro-adsorption can be broadly categorized as carbon-based (e.g., activated carbon, carbon cloth, graphite, carbon fibers, carbon felts, graphene), metal-based, and polymer/resin-based [60]. Among these, carbon-based electrode materials dominate the literature due to their widespread availability, relatively low cost, and favorable properties for electro-adsorption, such as high surface area, well-developed porosity, good conductivity, and electrochemical stability (especially under cathodic operating conditions). Graphene, characterized by its 2D honeycomb lattice of sp^2 -hybridized carbon atoms, has gained increasing interest in environmental electrochemistry owing to its unique structure and properties [61]. In contrast, metal-based electrodes have been less extensively studied, likely due to higher material costs and more limited tunability of surface area and porosity. However, their crystallographic orientation and surface electronic structure can significantly affect EDL formation and thus electro-adsorption performance [62].

3.2.2. Pore structure and its influence on EDL formation

High surface area and optimized pore-size distribution are crucial for enhancing charge accumulation at the electrode/electrolyte interface [63]. Chemical or thermal activation is commonly used to tailor these textural properties in carbon materials. Pore size has a direct impact on EDL characteristics: ~ 2 nm pores typically host standard EDL structures, 1–2 nm pores introduce confinement effects, and pores < 1 nm involve ion desolvation [64]. A hierarchical prediction model has been proposed to describe EDL formation across various porous architectures (Fig. 3): the sandwich model for micropores (< 2 nm), the double-cylinder model for mesopores (2–50 nm), and the planar model for macropores (> 50 nm) [65–67].

3.2.3. Interfacial properties

The electrical conductivity of electrode materials influences the rate of electron transfer at the material/electrolyte interface, while surface functional groups mainly contribute to specific adsorption interactions [68]. Wettability also plays a vital role, as poor wettability often hinders the transport of hydrophilic ions into porous structures, negatively impacting electro-adsorption efficiency; however, this factor is rarely quantified in existing electro-adsorption studies. Applied current polarity influences both the rate and capacity of electro-adsorption on porous surfaces. Reported polarity configurations in the literature are distributed approximately as cathodic (23%), anodic (41%), and bipolar (36%). Polarity must be carefully selected based on the charge characteristics of the target species, as polarity-induced electromigration can influence ion transport and overall adsorption performance.

4. Performance, mechanisms, and operational factors of REE electro-adsorption

Building upon the theoretical foundations discussed above, the following section focuses on the practical application of electro-adsorption, highlighting how these mechanistic principles translate into selective separation under complex aqueous environments. Unlike conventional methods, electro-adsorption has emerged as a promising green technology for REE recovery, especially under low-concentration and chemically complex conditions. Its non-Faradaic nature, environmental friendliness, and compatibility with various electrode materials make it an attractive alternative to conventional recovery methods. While the application of electro-adsorption in REE recovery is still in its early stages, most reported studies have focused on utilizing materials with high surface area, tunable porosity, and excellent electrical conductivity. Ultimately, the performance of this technology is governed by

the interplay between electrode surface chemistry and factors such as solution pH, applied voltage, and ionic background.

4.1. Carbon-based electrodes and their functional modifications

Carbon materials such as activated carbon and graphene are widely employed due to their hierarchical porous structures and high electrical conductivity. The remarkable versatility of carbon materials has been widely investigated to recover metals such as Li^+ , Cu^{2+} , and heavy metals, which are frequently encountered in environmental remediation and industrial recovery processes. For example, in capacitive deionization technologies, carbon-based electrodes have been widely studied for salt removal, where hierarchical pore structures and surface functional groups play a crucial role in ion adsorption [69]. These structural features enhance electrochemical performance by shortening diffusion pathways and increasing the electroactive surface area.

4.1.1. Pristine carbon-based electrodes and EDL dominance

In pristine carbon-based electrodes, REE recovery is governed by the EDL theory. For a mechanistic perspective, the adsorption of REEs on carbon surfaces can be described by the Modified Gouy-Chapman model, where the local concentration of ions at the electrode interface is exponentially related to their ionic charge. Owing to their trivalent nature, REEs experience significantly stronger electrostatic attraction toward the cathode compared to monovalent or divalent impurity ions. This results in a much higher packing density within the Stern layer, explaining the high selectivity of electro-adsorption for REEs, particularly in low-concentration and compositionally complex environments.

For instance, Engmann et al. [70] demonstrated the electro-adsorption of Nd^{3+} using carbon electrodes under a current density of 89.1 mA/g. Selectivity in electro-adsorption is commonly quantified using the selectivity factor (S), defined as the ratio of the distribution coefficients (K_d) of a target ion (A) relative to a competing ion (B):

$$S_{A/B} = \frac{K_{dA}}{K_{dB}} = \frac{(C_0/C_e)_A}{(C_0/C_e)_B} \quad (3)$$

High selectivity factors were achieved for Nd^{3+} over Li^+ (8.6), Na^+ (1.1), and Mg^{2+} (10.9), indicating strong preferential adsorption of trivalent REEs over background ions. The ion storage was found to rely more on pore structure than interlayer spacing. Zhang et al. [71] demonstrated nearly complete removal of REEs (< 10 mg/L) using activated carbon electrodes, further confirming the key role of porous architecture and EDL capacitance in achieving high selectivity under dilute conditions.

The performance of carbon-based electrodes is also critically dependent on operational parameters. Within an applied voltage window of 0–1.0 V (Fig. 4a), a higher applied potential generally correlates with increased adsorption capacity, as the strengthened electric field enhances EDL formation and ion accumulation [72,73]. The specific charge of ion adsorption (SQ in C/g) can be calculated by the following equation:

$$SQ = \frac{\int_0^t i(t) dt}{m_{ion}} \quad (4)$$

where $i(t)$ is the current at time t , and m_{ion} is the mass of adsorbed ions. At applied potentials above 1.0 V, adsorption capacity often plateaus, and potentials exceeding 1.2 V may induce side reactions like water electrolysis, which can reduce process efficiency.

Solution pH is another critical factor, as it influences both ionization and protonation of the electrode surface. Under strongly acidic conditions ($\text{pH} < 3.0$), protons (H^+) compete with REEs for active adsorption sites, thereby reducing efficiency [72]. As pH increases, proton competition diminishes, resulting in a sharp increase in adsorption capacity until a plateau is reached. Moreover, at a fixed number of active sites, increasing REE concentration leads to gradual saturation of the

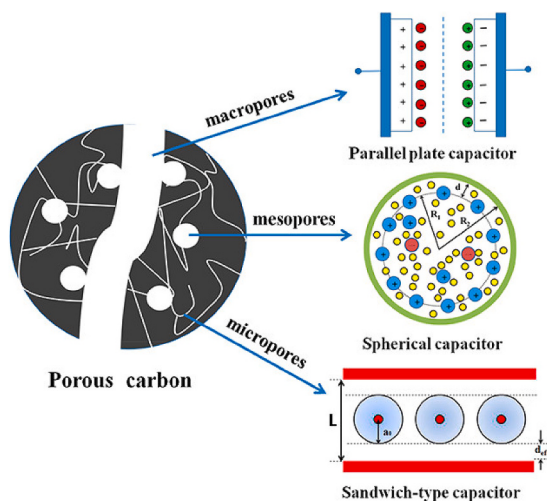


Fig. 3. Multi-scale model illustrating the influence of pore structure on EDL formation [65].

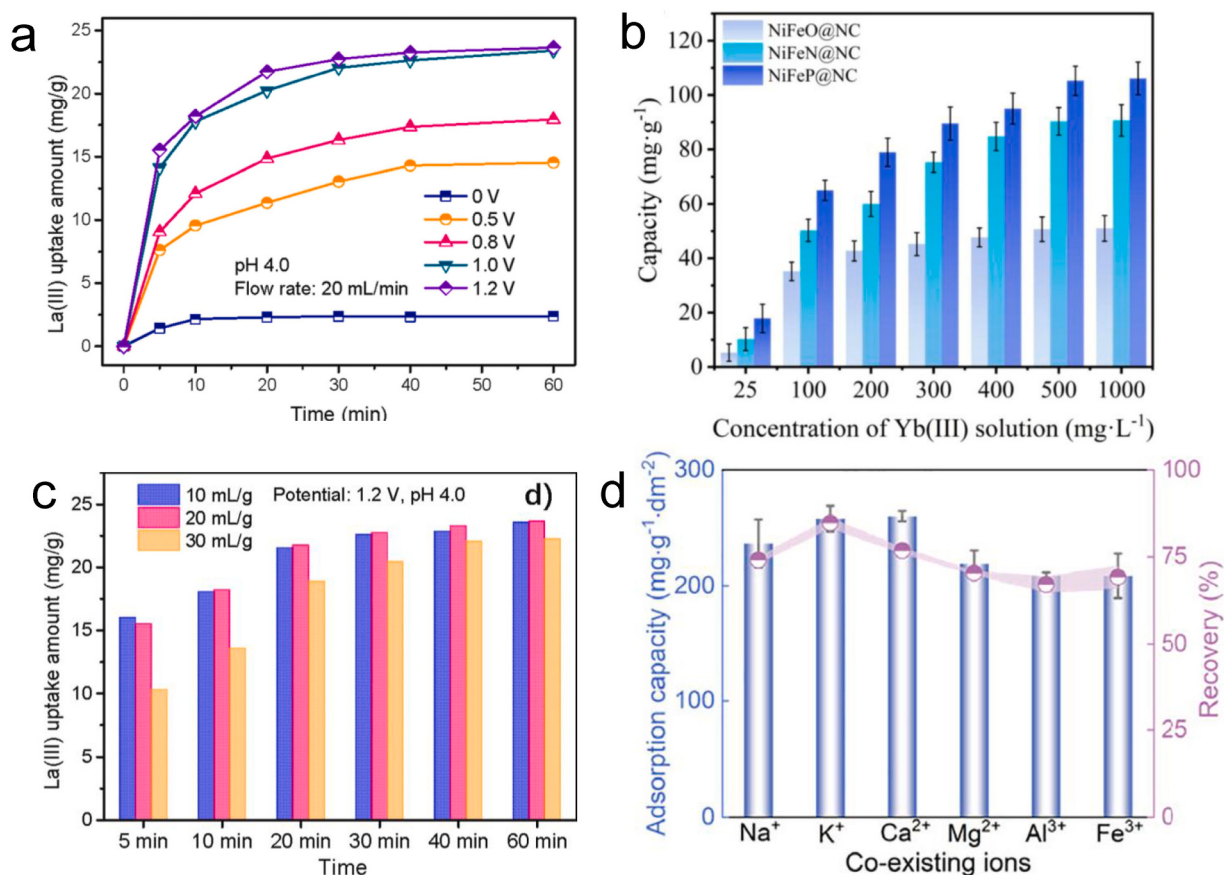
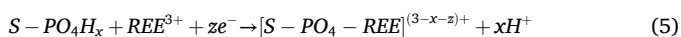


Fig. 4. Effect of (a) applied voltage and (c) flow rate on the electro-adsorption performance of La^{3+} using the pyrrolic-N doped activated carbon electrode [74]; (b) electro-adsorption capacities of Yb^{3+} at various initial concentrations using three different electrodes, highlighting material-specific uptake performance [73]; (d) influence of coexisting ions on the electro-adsorption efficiency and selectivity for La^{3+} [72].

adsorption surface (Fig. 4b), consistent with classical adsorption isotherm behavior. Flow rate (Fig. 4c), for instance, was found to have a relatively minor impact on REE uptake [74], likely due to the dominance of surface-controlled processes over mass-transfer limitations.

4.1.2. Heteroatom doped and chemical-electrochemical synergy

Heteroatom doping (e.g., nitrogen, oxygen, or sulfur) can further improve the hydrophilicity, conductivity, and redox activity of carbon materials [75]. Such modifications shift the dominant electro-adsorption mechanism from purely physical electrostatic attraction toward a chemical-electrochemical synergistic process. Based on hard-soft acid-base (HSAB) theory, REE ions are classified as “hard acids” with strong affinity for “hard bases” like oxygen-containing phosphate groups [76]. Surface complexation reaction can be described as:



This coordination bonding provides substantially higher binding energy than simple electrostatic attraction, enabling effective REE capture even in the presence of high-concentration background ions. For example, Zhao et al. [74] developed pyrrolic nitrogen-doped activated carbon that achieved a La^{3+} adsorption capacity of 23.66 mg/g within 25 min (Fig. 5a). Similarly, Zhang et al. [73] modified polydopamine-derived carbon spheres with Ni–Fe oxides, nitrides (Fig. 5b), or phosphides, achieving a Yb^{3+} adsorption capacity of 105.24 mg/g under low-voltage conditions. Despite a slight decrease in surface area, the introduction of redox-active sites significantly enhanced the electrochemical performance. Xiong et al. [77] synthesized phosphorus-doped carbon materials showing an 86% improvement in La^{3+} adsorption capacity relative to undoped carbon, attributed to selective La–O–P and $\text{P}_2\text{O}-\text{La}^{3+}$

bonding (Fig. 5c). The practical significance of this chemistry was further explored by Lin et al. [78], who investigated the selectivity of $\text{Mn}_3\text{O}_4@\text{PC}$ electrodes, as shown in Fig. 5d. Because trivalent REEs show stronger interactions and more favorable hydration energies compared to divalent or monovalent impurities, they demonstrate stronger adsorption competitiveness on functionalized electrodes, which is essential for recovering REEs from complex aqueous streams. Moreover, Ji et al. [79] synthesized Fe-doped $\text{CoS}_2@\text{NC}$ using polydopamine as a precursor, achieving a Yb^{3+} adsorption capacity of 129.4 mg/g within 60 min.

4.2. Pseudocapacitive materials for REE recovery

Pseudocapacitive materials like MoS_2 and metal oxides provide higher ion storage densities via Faradaic processes, such as intercalation and surface redox coupling [80]. In electro-adsorption systems where REE precipitation is observed, the dominant mechanism involves electrochemical reduction of water or dissolved oxygen, which generates localized alkalinity near the cathode surface. This regional supersaturation leads to the formation of REE hydroxides.

Wang et al. [81] used sodium diphenylamine sulfonate-modified carbon fibers to recover Nd^{3+} and Ce^{3+} , achieving adsorption capacities of 275 and 366 mg/g, respectively, after 180 min. The process led to the formation of distinct REE precipitates (Fig. 5e), including $\text{La}(\text{OH})_3$ (white flocculent solids), $\text{Nd}(\text{OH})_3$ (purple flakes), and CeO_2 (yellow spheres). In a subsequent study [82], graphene-based film electrodes enabled even higher adsorption capacities of La^{3+} (2510.5 mg/g), Nd^{3+} (2346.25 mg/g), and Ce^{3+} (2150.75 mg/g), as shown in Fig. 5f. These results highlight the significant contribution of Faradaic processes in

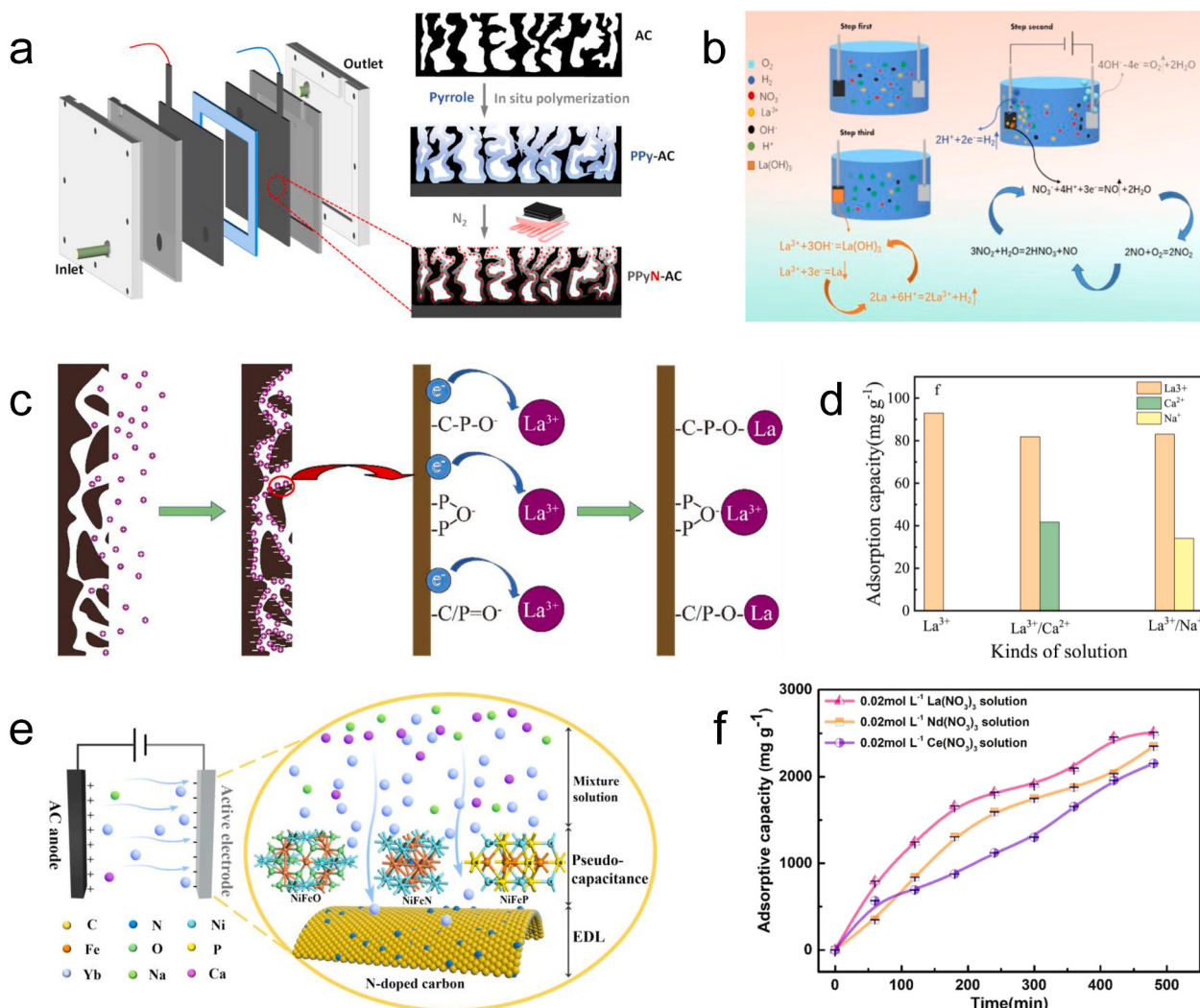


Fig. 5. (a) Schematic diagrams of a CDI module (left) and the synthesis of modified AC (right); (b) schematic representation of the adsorption-desorption cycle using the SDAS-AC-CF electrode; (c) mechanisms of electro-adsorption: EDL adsorption and Faradaic adsorption; (d) electro-adsorption selectivity of Mn₃O₄@PC composite electrodes; (e) proposed electro-adsorption mechanisms for three types of electrodes including bimetallic oxide, nitride, and phosphide on N-doped carbon spheres; (f) adsorption capacities for La³⁺, Nd³⁺, and Ce³⁺ using laser-induced graphene film electrodes.

pseudocapacitive carbon systems.

Beyond carbon-based materials, metal-based electrodes have also been extensively investigated due to their inherent redox activity and superior ion-sieving capabilities. For instance, a redox-active copolymer containing carboxylic acid and ferrocene units exhibited reversible Y³⁺ adsorption with a capacity of 69.4 mg/g [83]. Su et al. [84] utilized a 3D network of nickel foam to recover La, Nd, Ce, and Pr, benefiting from its excellent conductivity, porosity, and reusability. Their results confirmed that applied electric fields significantly enhance REE migration and precipitation. Furthermore, Zhan et al. [72] demonstrated that engineering specific binding sites on oxygen-doped MoS₂ electrodes can induce differential affinities among REEs with close physicochemical properties, thereby enhancing selectivity (Fig. 6a).

4.3. Membrane-coupled electrochemical systems for REE separation

Besides electrode-based recovery, membrane-assisted electrochemical systems are also emerging as effective platforms for REE recovery. In rare earth mining effluents, coexisting contaminants such as ammonium nitrogen (NH₄⁺) pose additional challenges [85]. Conventional biological processes are often ineffective due to high salinity, REE toxicity, and limited availability of biodegradable carbon sources.

Electrochemical oxidation provides a reagent-free solution for ammonia degradation and is particularly compatible with highly mineralized wastewater, as it does not require the addition of supporting electrolytes [86]. However, standalone electrochemical processes are generally insufficient for REE recovery, often requiring integration with electrocoagulation and membrane separation [87]. Lin et al. [88] developed a hybrid ceramic membrane system that integrates electrocoagulation, electrooxidation, and membrane separation for deep REE recovery (Fig. 6d). Under optimized operating conditions, this integrated system achieved removal efficiencies of 99.84–99.98% for both REEs and ammonium nitrogen, providing a scalable approach for mine wastewater treatment.

To facilitate comparison across different electrode materials, representative performance data from the literature are summarized in Table 2. This table highlights targeted REEs, adsorption capacities, and corresponding recovery efficiencies for each electrode. As shown, carbon-based electrodes remain the most extensively studied due to their low cost and wide availability. However, their limited selectivity toward specific REE ions has prompted the development of alternative materials, such as sulfide-, nickel-, and titanium-based electrodes, which have demonstrated enhanced selectivity and recovery performance. Nevertheless, challenges related to long-term stability, cycling

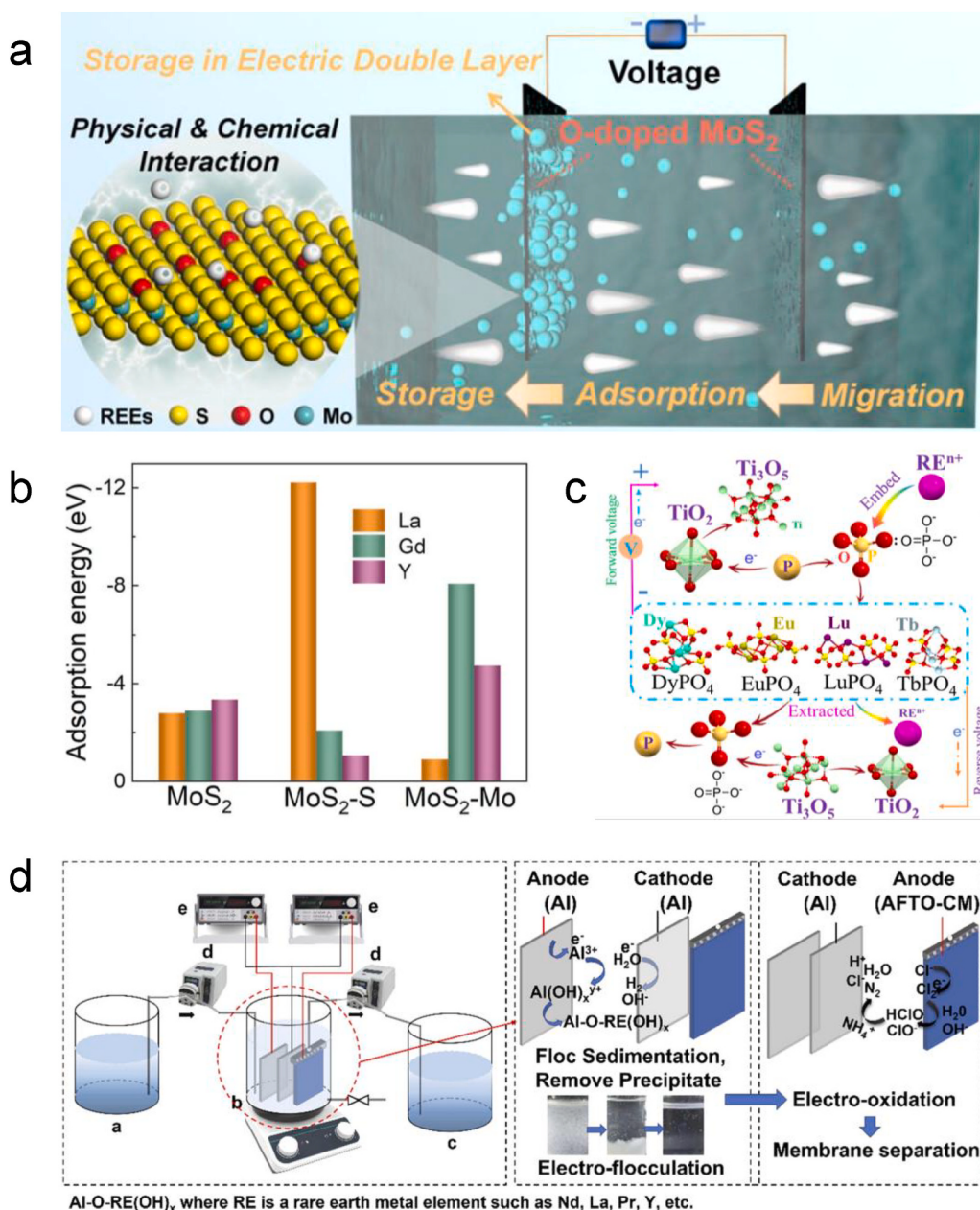


Fig. 6. (a) Electro-adsorption process for REEs and regulation of physical and chemical interaction on electrodes [72]; (b) adsorption energies of La³⁺, Gd³⁺, and Y³⁺ on pristine MoS₂, Mo-defect MoS₂, and S-defect MoS₂ [89]; (c) schematic representation of the capacitive recovery process of REEs on the TiO₂/P/C electrode surface, emphasizing the role of phosphorus modification in enhancing electro-adsorption efficiency [90]; (d) diagram of an integrated treatment system combining electro-flocculation, electro-oxidation, and membrane separation for rare earth mine wastewater [88].

durability, and cost-effectiveness remain and must be addressed to enable practical deployment.

4.4. Environmental and techno-economic considerations

Compared with conventional separation methods such as precipitation, solvent extraction, and membrane filtration, electro-adsorption offers distinct advantages in terms of sustainability and cost-efficiency. From an environmental perspective, electro-adsorption is essentially a “reagent-free” technology that eliminates the need for corrosive organic extractants, excessive chemical precipitants, and disposable polymeric membranes. Consequently, this approach significantly reduces secondary waste generation and mitigates the environmental hazards associated with traditional hydrometallurgical reagents.

Economically, electro-adsorption operates under mild conditions,

which reduces the requirement for specialized, corrosion-resistant infrastructure. Furthermore, the ability to regenerate and reuse electrode materials contributes to lower operational expenses. Preliminary assessments suggest that electro-adsorption may offer lower long-term costs than conventional technologies, particularly when treating dilute and compositionally complex waste streams where solvent loss or reagent consumption would otherwise be economically prohibitive. However, it is important to emphasize that detailed techno-economic analysis (TEA) and life cycle assessment (LCA) specifically for REE electro-adsorption are currently not available in the existing literature.

Despite these advantages, several challenges hinder the broader application of electro-adsorption for REE recovery. Long-term electrode durability remains a critical issue, as repeated electrochemical cycling may cause surface fouling, gas evolution, or structural degradation that compromises performance. Energy consumption, while generally lower

Table 2

Summary of reported electrodes used for REE recovery, including adsorption capacity and recovery.

Electrodes	REEs	Adsorption capacity (mg/g)	Recovery (%)	Ref.
Carbon	Nd ³⁺	125	/	[70]
Pyrrolic-N doped activated carbon electrodes	La ³⁺	23.66	/	[74]
NiFeN@NC	Yb ³⁺	90.31	/	[73]
Phosphorus doping porous carbon	La ³⁺	140	94.08	[77]
Mn ₃ O ₄ -loaded phosphorus-doped porous carbon	La ³⁺	93.02	89.27	[78]
Sodium diphenylamine sulfonate modified activated carbon electrode	La ³⁺	600	/	[81]
Graphene film	Nd ³⁺	275	/	
	Ce ³⁺	366	/	
	La ³⁺	2510.5	/	[82]
	Nd ³⁺	2349.5	/	
	Ce ³⁺	2150.75	/	
Fe-CoS ₂ @N-doped carbon	Yb ³⁺	129.4	98	[79]
Nickel foam	La ³⁺	1347.7	/	[84]
	Nd ³⁺	841.9	/	
	Ce ³⁺	810.7	/	
	Pr ³⁺	1082	/	
Phosphorus-modified TiO ₂	Dy ³⁺	/	99.95	[90]
	Eu ³⁺	/	99.94	
	Tb ³⁺	/	99.93	
	Lu ³⁺	/	99.96	
Oxygen-doped molybdenum disulfide	La ³⁺	65.82	100	[72]
Defect-engineered molybdenum disulfide	Gd ³⁺	/	100	[89]
Activated carbon	La ³⁺	61.63	100	[71]

than that of conventional thermal processes, still requires optimization, especially for large-scale or continuous-flow systems. Moreover, maintaining high selectivity in complex aqueous matrices containing competing ions remains a key technical challenge, as such species commonly coexist with REEs in industrial effluents.

5. Separation of REEs from coexisting impurities

The separation performance of electro-adsorption exhibits distinct trends both among different REEs and between REEs and impurity ions (Fig. 4d) [90]. This highlights the importance of optimizing electrode surface chemistry and electrochemical conditions to enhance REE selectivity in complex solution systems. In REE electro-adsorption processes, separation performance is strongly influenced by ion valency and electrostatic interactions between ions and electrode surfaces. As mentioned in previous sections, trivalent REEs, such as La³⁺, show stronger electrostatic interactions and more favorable hydration energies compared to divalent or monovalent impurities (e.g., Li⁺, Na⁺, Mg²⁺, Ca²⁺) [72]. These stronger interactions lead to higher adsorption affinity for trivalent REEs on functionalized or doped electrodes, thereby enabling more efficiency separation from background ions. For example, Lin et al. [78] investigated the selectivity of Mn₃O₄@PC electrodes for La³⁺ in the presence of Na⁺ and Ca²⁺ and found that La³⁺ exhibited a significantly higher adsorption capacity than the competing ions. This result demonstrates that La³⁺ has a stronger adsorption competition ability under electro-adsorption conditions, a crucial attribute for practical applications in separating REEs from waste streams containing multiple metal ions.

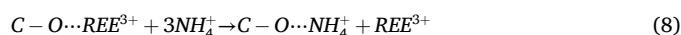
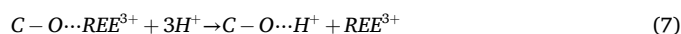
Despite this advantage, separating individual REEs with similar charge and ionic radius remains highly challenging due to the lanthanide contraction, which results in overlapping hydration energies and coordination behaviors. Recent studies (Fig. 6b) suggest that tailoring electrode surface chemistry (e.g., oxygen/phosphorus doping or defect engineering) can tune the chemisorption affinity to recognize subtle differences and create differential binding sites, thereby enhancing selectivity among REEs with close physicochemical properties [89].

These findings indicate that future optimization of electro-adsorption systems should not only focus on improving overall uptake capacity, but also on rational design of electrode architectures capable of discriminating structurally similar REEs while mitigating the competitive effects of coexisting impurity ions.

6. Desorption and reusability of electro-adsorption systems

For practical industrial applications, the ability to efficiently desorb captured REEs and maintain long-term electrode reusability is as critical as achieving high initial adsorption capacity. Desorption is typically achieved through electrochemical or chemical means. The most common approach is potential reversal, which utilizes electrostatic repulsion to drive REE ions away from the electrode surface. For instance, Zhang et al. [73] and Ji et al. [79] demonstrated that reversing the applied potential enables rapid ion release into a concentrated eluent stream. Interestingly, the high charge density of trivalent REEs can induce inter-ionic repulsion under a reversed electric field, further accelerating the desorption rate [79].

For materials involving strong chemisorption or surface complexation, electrochemical desorption alone may be insufficient. In such cases, chemical regenerants like HCl, NH₄Cl, or EDTA are commonly employed. Zhang et al. [71] compared HCl and NH₄Cl for La³⁺ desorption from carbon-based electrodes, finding that HCl achieved >90% desorption efficiency within 20 min, whereas NH₄Cl offered better electrode stability over repeated cycles. Chemical desorption typically proceeds via ion exchange or proton displacement mechanisms, as shown in the following equations [71]:



The structural integrity of electrodes during multiple adsorption-desorption cycles is a key determinant of the process economics. While several carbon-based electrodes like PPyN-AC and Fe-CoS₂@NC exhibit high capacity retention over multiple cycles, some composite materials show a “first-cycle drop”. For example, Mn₃O₄@PC [78] and Ni-Fe [73] bimetallic electrodes experienced a capacity decrease in early cycles due to irreversible binding at strongly active sites where REE ions were immobilized. Structural characterization using techniques such as X-ray diffraction (XRD) and Raman has confirmed that materials like MoS₂ [72] and activated carbon [71] maintain stable crystal structures after repeated cycling. Furthermore, ICP analysis is essential to monitor potential leaching of electrode components and ensure compliance with environmental discharge standards. Notably, Mao et al. [90] reported that TiO₂/P/C electrodes (Fig. 6c) maintained >99% REE recovery efficiency even after 100 cycles, achieving approximately 90-fold enrichment, underscoring the potential for large-scale continuous operation.

7. Challenges and future perspectives

The development of electro-adsorption technologies for REE recovery shows considerable promise, particularly for low-concentration and compositional complex aqueous systems. However, several challenges must be addressed before this approach can be broadly deployed in industrial settings. Electro-adsorption performance is fundamentally governed by EDL formation and ion transport, both of which are collectively dictated by the structural and surface chemistry of electrode materials, as well as the operating conditions (e.g., applied voltage, pH, and electrolyte concentration).

7.1. Sustainability and techno-economic viability

The industrial transition of electro-adsorption for REE recovery is

contingent upon its ability to achieve favorable economic performance while maintaining a reduced environmental footprint. Compared with conventional solvent extraction, which relies on large volumes of organic solvents and chemical saponification, electro-adsorption is inherently a “reagent-free” technology that primarily utilizes electrons as the primary driving force. This feature substantially reduces secondary waste generation and associated environmental risks. From a cost perspective, the operational expenditures of electro-adsorption are predominantly governed by energy consumption and electrode lifespan. The capital costs remain high due to the use of advanced electrode materials like graphene or specialized metal-organic frameworks. Future research should prioritize LCA and TEA to quantify carbon intensity, material durability, and long-term cost competitiveness, ensuring that the environmental advantages of electro-adsorption translate into viable commercial alternatives.

7.2. Electrode material design

Electric conductivity, surface wettability, and pore structure are key factors influencing electro-adsorption efficiency as shown in Fig. 7. High conductivity allows for rapid charge transfer, while hydrophilic surfaces improve electrolyte penetration and promote effective contact between active sites and target ions. Pore size distribution plays a critical role in EDL, especially mesopores, which facilitate ion diffusion, reduce internal resistance, and improve adsorption kinetics. Developing composite electrodes that balance these properties will be essential for enhancing system performance. Compared with electro-adsorption systems optimized for other ions such as Li^+ and Au^{3+} , the recovery of REEs faces unique challenges stemming from their multivalent nature and higher charge density. Although certain materials exhibit excellent selectivity and capacity in other applications, their implementation in REE systems is often hindered by insufficient cycling stability and high operational costs. Therefore, lessons learned from these advanced materials, such as the integration of redox-active functional groups, hierarchical pore architectures, and defect engineering, could inspire next-generation electrode designs for efficient and selective REE recovery. At present, quantitative understanding of the correlation between electrode microstructure and charge-transfer dynamics remains limited. Future research should focus on combining in situ spectroscopy analyses and computational modeling to unravel these structure-property relationships and guide rational materials design.

7.3. Integration with other processes

Combining electro-adsorption with other treatment methods presents a promising route to improve selectivity and overall system

performance. For instance, integrating photoelectrochemical oxidation or membrane filtration can help remove coexisting impurities cations like ammonium or organic contaminants, which can otherwise influence the ionic strength and coordination chemistry of the solution, thereby enhancing REE separation. Membrane-assisted systems may also improve energy efficiency and reduce the need for chemical additives. Future studies are needed to assess synergistic effects and energy efficiency under real wastewater conditions, as most current demonstrations are limited to model systems.

7.4. Material sustainability & anode utilization

Developing low-cost, scalable, and environmentally friendly electrode materials remains foundational to industrial adoption. Promising candidates include biomass-derived carbons, heteroatom-doped porous frameworks, and hybrid metal oxide-carbon composites, with synthesis routes guided by green-chemistry principles to ensure long-term economic and environmental feasibility. Additionally, although most current REE-focused electro-adsorption studies have mainly emphasized cathode design, the role of the anode is often overlooked. Drawing on insights from electro-adsorption systems developed for other metal ions, anodes may be strategically engineered to simultaneously degrade nitrogen-containing contaminants commonly present in REE-bearing leachates, thereby improving overall system efficiency and sustainability.

7.5. Current efficiency & product recovery

Optimizing current efficiency is essential. Minimizing side reactions, particularly water electrolysis at higher voltages, can reduce energy losses and enhance sustainability. Careful tuning of applied voltage and current density can maintain high adsorption performance without sacrificing energy efficiency. In terms of recovery, capturing REEs as solid phases instead of re-dissolving them into eluates offers a more direct and sustainable pathway. However, this requires precise control over nucleation and precipitation conditions to achieve high-purity products.

7.6. System scaling & reactor engineering

Finally, most research relies on small-scale batch laboratory setups using simple parallel-plate or three-electrode configurations, which fail to reflect the complexities of real-world industrial environments. Future development must prioritize the transition from batch circulation to modular stack designs to significantly increase treatment capacity. Furthermore, replacing batch systems with single-pass flow-through

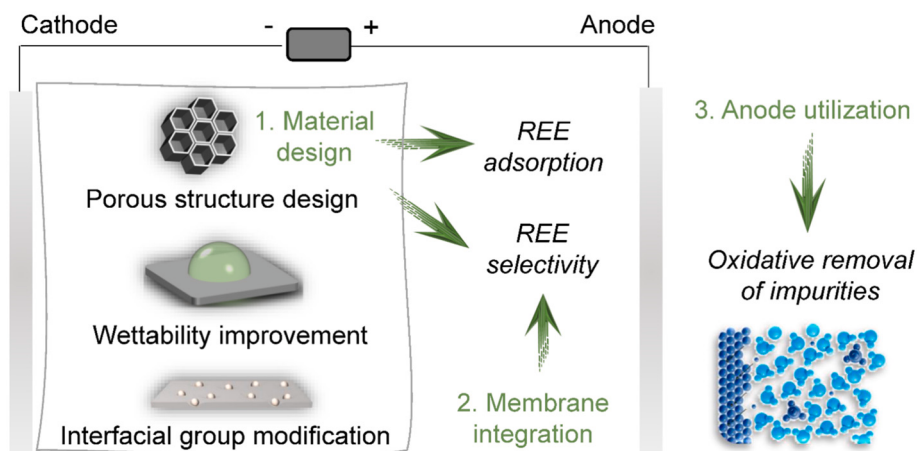


Fig. 7. Future development directions for electro-adsorption of REEs.

reactors or continuous flow-electrode CDI is essential for enabling high-throughput REE recovery. Beyond standard rectangular modules, exploring alternative reactor geometries, such as cylindrical or tubular electrochemical cells, may offer superior control over fluid dynamics and ensure more uniform current distribution. Moving toward these semi-continuous or continuous configurations will be critical for assessing scalability, operational reliability, and long-term cost-effectiveness while addressing practical engineering challenges such as electrode fouling and current leakage.

8. Conclusions

This review highlights the potential of electro-adsorption as a sustainable and selective technology for the recovery of REEs from dilute and compositional complex aqueous systems. Unlike traditional methods, electro-adsorption offers the combined benefits of non-Faradaic and Faradaic processes, tunable selectivity, and minimal chemical input. The efficiency of this method is largely governed by the interplay between EDL formation and mass transfer, both of which are influenced by electrode material design and solution chemistry.

Recent advances have shown that porous carbon-based materials with appropriate surface functionalities and hierarchical pore structures can achieve high adsorption capacities. Heteroatom doping and surface modification further enhance adsorption performance through improved conductivity, wettability, and the introduction of redox-active sites. Specifically, this review concludes that while electro-adsorption is highly efficient for separating REEs from non-REE impurities based on valency differences, the selective discrimination between individual REEs remains the primary bottleneck. Additionally, combining electro-adsorption with other treatment technologies has shown promise in extending its applicability to multi-contaminant systems.

Despite these advances, significant challenges remain for practical deployment. Scale-up limitations, suboptimal current efficiency, electrode degradation under repeated cycling, and diminished selectivity in the presence of competing ions continue to hinder industrial adoption. In addition, robust strategies for regenerating electrodes and transforming adsorbed REEs into market-ready products are still underdeveloped. Finally, pilot-scale demonstrations using realistic leachates are urgently needed to assess energy efficiency, operational costs, and scalability.

Looking forward, future research should prioritize the development of multifunctional electrode materials and integrated system designs that simultaneously address selectivity, durability, and sustainability. Transitioning from laboratory-scale studies to scalable, continuous-flow electrochemical systems will be critical for translating electro-adsorption into viable industrial solutions for REE recovery. Moreover, synergistic advances in materials innovation and process integration will be essential to overcoming current limitations and achieving the full potential of electro-adsorption for REE recovery.

CRediT authorship contribution statement

Wei quan Zhan: Writing – review & editing, Writing – original draft.
Wencai Zhang: Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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