

Review

Electro-Driven Membrane Separations for Sustainable Bio-Based Chemical Recovery: Energetics, Selectivity Engineering, Scale-Up Challenges, and Industrial Translation

Akeem Adeyemi Oladipo 

Polymeric Materials Research Laboratory, Chemistry Department, Faculty of Arts and Science,
Eastern Mediterranean University, TR North Cyprus, via Mersin 10, Famagusta 99628, Türkiye;
akeem.oladipo@emu.edu.tr

Abstract

The economic viability of circular biorefineries is fundamentally constrained by the energetic and thermodynamic limits of conventional downstream processing. This critical review examines the paradigm shift toward electro-driven membrane separations, establishing them not merely as alternative filtration devices, but as active, programmable electrochemical interfaces. Moving beyond classical bulk-desalination models, the analysis elucidates the complex reactive-transport physics governing bio-based chemical recovery, where localized pH modulation, electrostatic gating, and field-induced speciation dictate molecular discrimination. The manuscript critically benchmarks the inescapable macro-scale thermodynamic tradeoff among interfacial selectivity, volumetric productivity, and specific energy consumption (kWh/kg). Furthermore, it evaluates the integration of active 2D nanoconfined materials (e.g., MXenes) and rigorously critiques the severe performance degradation modes—specifically electro-biologically coupled fouling and anodic oxidation—that paralyze industrial scale-up. Ultimately, this review outlines a strategic mandate for the fully electrified biorefinery, where continuous in situ product recovery, artificial intelligence-guided module design, and autonomous cyber-physical control systems converge to eliminate legacy thermal unit operations and seamlessly integrate biomanufacturing with decarbonized electrical grids.

Keywords: electrified membranes; electrodialysis; bipolar membrane electrodialysis; bio-based chemicals; selective transport; resource recovery; circular bioeconomy

1. Introduction

The transition from a fossil-based economy to a circular bioeconomy has fundamentally redefined the role of separation technologies. Modern biorefineries can now convert diverse renewable feedstocks—ranging from lignocellulosic biomass to industrial organic waste—into an expansive portfolio of platform chemicals, organic acids, biofuels, and specialty bioproducts [1,2]. Yet, the commercial viability of these processes is rarely constrained by the efficiency of upstream biological conversion; rather, it is dictated by the complexity of downstream recovery. In contemporary fermentation routes, downstream processing routinely accounts for 50–80% of total manufacturing costs and specific energy consumption [3,4]. Consequently, separation has emerged as the principal bottleneck impeding the scalable industrial deployment of bio-based chemical production.

This bottleneck is a direct consequence of the intrinsic thermodynamic and physico-chemical properties of biological streams. Unlike traditional desalination or wastewater



Academic Editor: Svetlozar Velizarov

Received: 15 June 2026

Revised: 15 July 2026

Accepted: 16 July 2026

Published: 18 July 2026

Copyright: © 2026 by the author.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

treatment, where the objective is bulk deionization of predictable electrolytes, bio-based matrices are highly complex, dilute mixtures. They contain weak acids, zwitterionic compounds, uncharged solvents, microbial metabolites, and biopolymers [5,6]. Crucially, the target molecules within these streams exhibit dynamic physicochemical states that continuously shift in response to local pH, ionic strength, and competitive binding. The coexistence of chemically similar species with nearly identical molecular weights renders conventional size-based or hydraulic separations insufficient for achieving the dual mandates of high purity and high recovery [7].

Traditional downstream architectures—including distillation, evaporation, and pressure-driven membrane filtration—were engineered for commodity chemical production under relatively predictable feed conditions. Applying these legacy technologies to dilute biologically derived streams incurs severe thermodynamic penalties. Thermal processes face the fundamental limitation that energy consumption scales with the high latent heat of vaporization of the bulk water, rather than the mass of the dilute target molecule [8,9]. Similarly, pressure-driven membranes rely almost exclusively on steric hindrance and hydraulic permeability, offering no mechanistic control over molecules that exhibit comparable dimensions but radically different charge states or chemical functionalities [10]. The result is a rigid tradeoff among separation efficiency, chemical dosing (for pH adjustment or precipitation), and operational cost, which fundamentally undermines the economic and environmental value proposition of sustainable biorefining.

These limitations have catalyzed a profound conceptual shift toward electrification as the new paradigm for molecular separation. Rather than relying on hydraulic pressure or thermal gradients, electro-driven membrane systems introduce electric fields as programmable driving forces. Under an applied electric field, the membrane transitions from a passive physical barrier into an active, responsive interface where local pH, charge distribution, and electrochemical potential collectively dictate molecular transport [11,12]. Separation is no longer a macroscopic sieving process; it becomes the precise manipulation of molecular interactions.

This paradigm is exceptionally powerful for bio-based recovery because it directly exploits the dynamic nature of biological molecules. Weak organic acids, amino acids, and fermentation intermediates continuously transition between protonated and deprotonated states. By coupling electrochemical potential gradients with local pH environments, electrified interfaces induce speciation shifts that actively govern transport. Selective migration emerges from the interplay of Donnan exclusion, interfacial partitioning, proton-coupled transport, and field-induced speciation [13–15]. Consequently, the electrified membrane functions as a programmable molecular decision layer, selectively extracting target compounds while actively suppressing competitive transport.

Despite rapid technological advancement, the current literature surrounding electro-driven bioseparations remains conceptually fragmented. Existing reviews predominantly emphasize isolated architectural descriptions—treating electrodialysis, bipolar membranes, and capacitive systems as disjointed subjects—or present descriptive catalogues of membrane polymers without establishing their fundamental mechanistic relationship to transport physics [12,16,17]. More critically, the foundational distinction between desalination-oriented transport and bio-based recovery is frequently overlooked.

Performance metrics and scaling laws established for the bulk transport of simple inorganic salts (e.g., Na^+ , Cl^-) cannot be directly extrapolated to the recovery of structurally diverse, sterically hindered organic molecules [12]. Furthermore, the defining engineering constraint of these systems—the fundamental macroscopic tradeoff among molecular selectivity, system productivity, and specific energy consumption—has received remarkably little systematic analysis.

To explicitly position this manuscript within the broader literature and delineate its novelty, Table 1 systematically benchmarks this work against recent, highly cited reviews in the field. Unlike previous studies that either treat specific electro-separation modalities in isolation (such as focusing solely on capacitive deionization or diffusion dialysis) or focus exclusively on specific waste streams and bulk inorganic deionization, this review bridges the critical gap between reactive-transport physics at the membrane interface and system-level biorefinery economics. To ensure a rigorous and transparent review methodology, a systematic literature retrieval was executed across the Web of Science, Scopus, and PubMed databases (spanning 2015–2026). The search employed Boolean strings combining primary electro-separation modalities (“electrodialysis” OR “bipolar membrane” OR “capacitive deionization” OR “bioelectrochemical systems”) with target biorefinery applications (“biorefinery” OR “fermentation” OR “organic acid recovery” OR “bioproduct processing”). From an initial pool of over 480 screened abstracts, approximately 185 empirical studies were selected. To prioritize industrial relevance over simple proof-of-concept demonstrations, studies were evaluated against explicit inclusion criteria: the reporting of complete thermodynamic driving forces, standardized specific energy consumption ($\text{kWh/kg}_{\text{product}}$), and clear feed matrix characterization that distinguishes idealized synthetic models from raw industrial broths.

Table 1. Comparative positioning of this review against recently published literature on electro-driven membrane technologies and biorefinery separations.

Refs.	Primary Scope and Focus	Target Compound Classes Covered	Key Analytical Limitations of Previous Reviews	Differentiating Contributions of This Work
[12]	Electro-membrane processes (ED, EDBM, EDI) and stack configurations for organic acid recovery from fermentation broths.	Organic acids (lactic, succinic, citric, acetic, and formic acids).	Focuses primarily on recovery yields, energy consumption, and conventional stack modifications; lacks comprehensive reactive-transport physics and life-cycle assessment (LCA) modeling.	Couples mathematical reactive-transport physics with a standardized empirical performance matrix and comprehensive TEA/LCA system boundaries, advancing beyond basic stack configuration studies.
[18]	Diffusion dialysis (DD) utilizing anion exchange membranes (AEMs) for acid recovery, including integration with pressure or electric fields.	Inorganic acids (e.g., HCl, H ₂ SO ₄) and toxic metal ion complexes from metallurgical and industrial waste.	Confined strictly to concentration-gradient-driven diffusion dialysis and bulk inorganic waste; lacks coverage of multi-modal electro-driven systems and bio-organic recovery.	Establishes a foundational distinction between bulk inorganic deionization and steric/speciation-controlled organic recovery in complex biorefinery streams.
[19]	Selective ion separation via capacitive deionization (CDI), emphasizing electrode material development and ion storage mechanisms.	Valuable metal ions, inorganic salts, and specific target ions (nitrate, phosphate, heavy metals).	Focused heavily on material-level mechanisms (e.g., EDLs, Faradaic reactions) without full integration into continuous fermentation loops or circular biorefinery economics.	Synthesizes CDI alongside other electro-driven membrane systems (EDMS) into a unified taxonomy based on thermodynamic driving forces and UN Sustainable Development Goal (SDG) alignment.
[20]	Electrodialysis and modified processes for nutrient recovery from anaerobic liquid digestate, alongside membrane fouling analysis.	Nutrients (nitrogen, phosphorus, potassium) and volatile fatty acids (VFAs).	Geared specifically toward anaerobic digestate treatment; lacks comprehensive modeling of multi-scale membrane degradation across a wider array of biorefinery platform chemicals.	Incorporates multi-scale degradation mechanics (e.g., anodic oxidation, binder dissolution) and expands the techno-economic framework to closed-loop biorefinery integration.

Table 1. Cont.

Refs.	Primary Scope and Focus	Target Compound Classes Covered	Key Analytical Limitations of Previous Reviews	Differentiating Contributions of This Work
This Review	Integrated electro-driven membrane systems (EDMS) for circular biorefineries.	Weak organic acids, amino acids, peptides, VFAs, nutrients, and platform chemicals.	N/A (Comprehensive systems-level critical review).	Couples mathematical reactive-transport physics with a standardized empirical performance matrix, TEA/LCA system boundaries, and an AI-guided autonomous control framework.

Addressing these gaps requires a framework that transcends standard technology classification. Accordingly, this review examines electro-driven membrane separations through the unifying perspective of molecular selectivity engineering and system energetics. Moving systematically across scales—from the molecular transport physics of electrified interfaces to macro-scale biorefinery integration—the analysis reconstructs how electric fields manipulate complex aqueous streams. Emphasis is placed on the mechanisms driving coupled ion–molecule transport, the nanoengineering of selective and stimuli-responsive membrane materials, and the targeted recovery pathways for distinct biochemical classes.

Crucially, this review establishes a critical benchmarking framework, rigorously evaluating the techno-economic performance, thermodynamic sustainability, and physical scaling constraints (e.g., complex biofouling, electrochemical degradation) that dictate industrial translation. Finally, emerging frontiers encompassing artificial intelligence-guided membrane design, autonomous process control, and fully electrified continuous biomanufacturing loops are identified.

Ultimately, this review argues that electro-driven membranes must no longer be viewed merely as alternative filtration devices. They are active electrochemical platforms necessary to transform downstream processing from a rigid, energy-intensive purification step into an adaptive, highly selective resource recovery engine. Mastering the dynamics of these electrified interfaces is not merely an incremental optimization; it is a fundamental prerequisite for realizing the economically viable, fully decarbonized biorefinery. This fundamental trajectory—transitioning from legacy pressure-driven macroscopic filtration toward programmable, electro-selective interfaces—is conceptualized in Figure 1, illustrating how electrification elevates the membrane from a passive physical barrier into an active engine for precision molecular recovery.

To maintain conceptual clarity and terminology consistency throughout this comprehensive analysis, all architectures utilizing applied electrical fields to drive selective molecular transport across membrane interfaces—including conventional electrodialysis, bipolar membrane configurations, capacitive deionization, and bioelectrochemical systems—are collectively defined and referred to hereafter as “electro-driven membrane systems” (EDMS). Furthermore, terms such as “programmable selectivity” and “active transport” are used strictly to describe the tunable physicochemical and thermodynamic mechanisms occurring at the electrified interface, rather than implying inherent computational hardware within the membrane material itself.

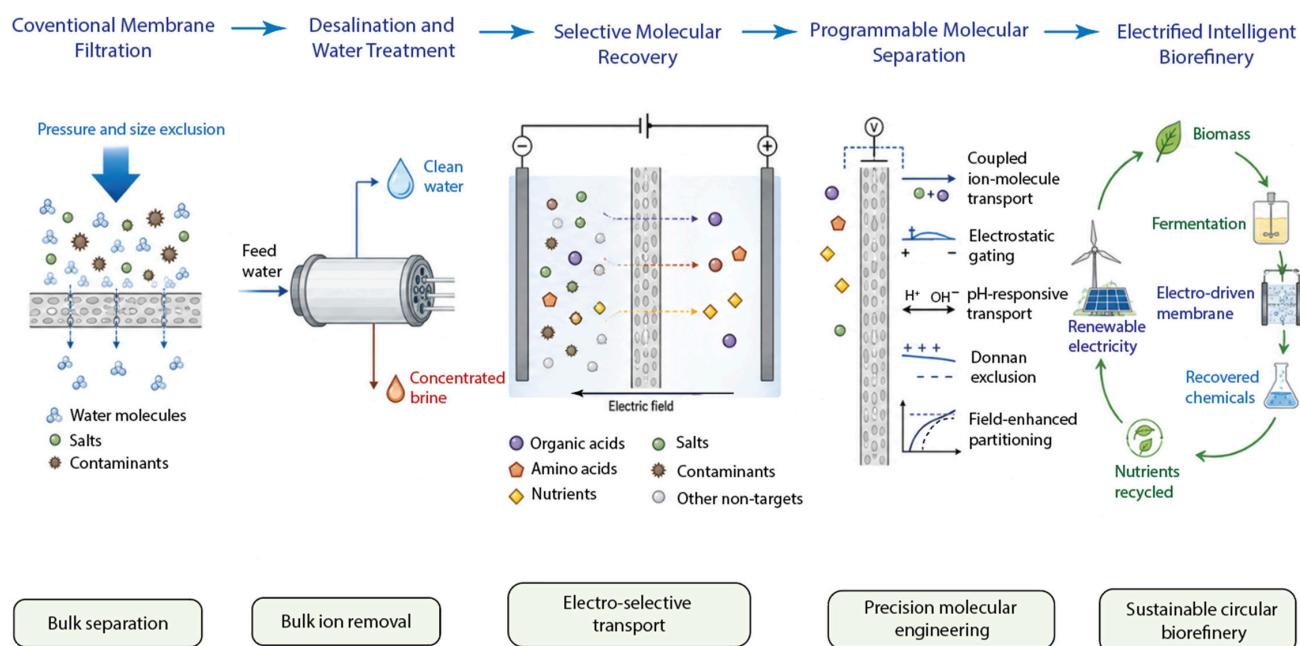


Figure 1. The evolutionary paradigm shift in membrane separations: transitioning from passive, pressure-driven bulk filtration to programmable electrochemical interfaces, culminating in the fully integrated, closed-loop electrified biorefinery.

2. Molecular Transport Physics and Selectivity Engineering in Electrified Membranes

The transition from conventional membrane filtration to electro-driven bioseparation requires a fundamental shift in understanding how molecular transport is governed. Classical membrane theories largely describe separation as a consequence of hydraulic pressure acting through polymeric free volume, where steric hindrance and passive diffusional resistance dictate performance [21,22]. While effective for desalination, this physical sieving paradigm is profoundly inadequate for recovering bio-based chemicals. Biological matrices contain molecules whose physicochemical properties evolve dynamically in response to local pH, ionic strength, and localized electric fields.

Under an applied voltage, the membrane is transformed into an active electrochemical environment where molecular migration is dictated by the simultaneous coupling of electromigration, proton transfer, and field-induced interfacial partitioning. Consequently, *interfacial selectivity* is not an intrinsic, static material property; it is an emergent thermodynamic phenomenon. The membrane functions as a programmable molecular decision layer capable of modulating activation energy barriers, rather than simply rejecting solutes based on hydrodynamic radius.

Figure 2 conceptually maps this interconnected framework—illustrating how electric fields manipulate local speciation to dictate transport pathways and energy consumption—while Table 2 synthesizes the specific interfacial selectivity mechanisms that exploit these phenomena. Moving beyond the macroscopic optimization of ionic conductivity, the fundamental challenge of modern electro-separations is engineering precise molecular discrimination under non-equilibrium electrochemical conditions.

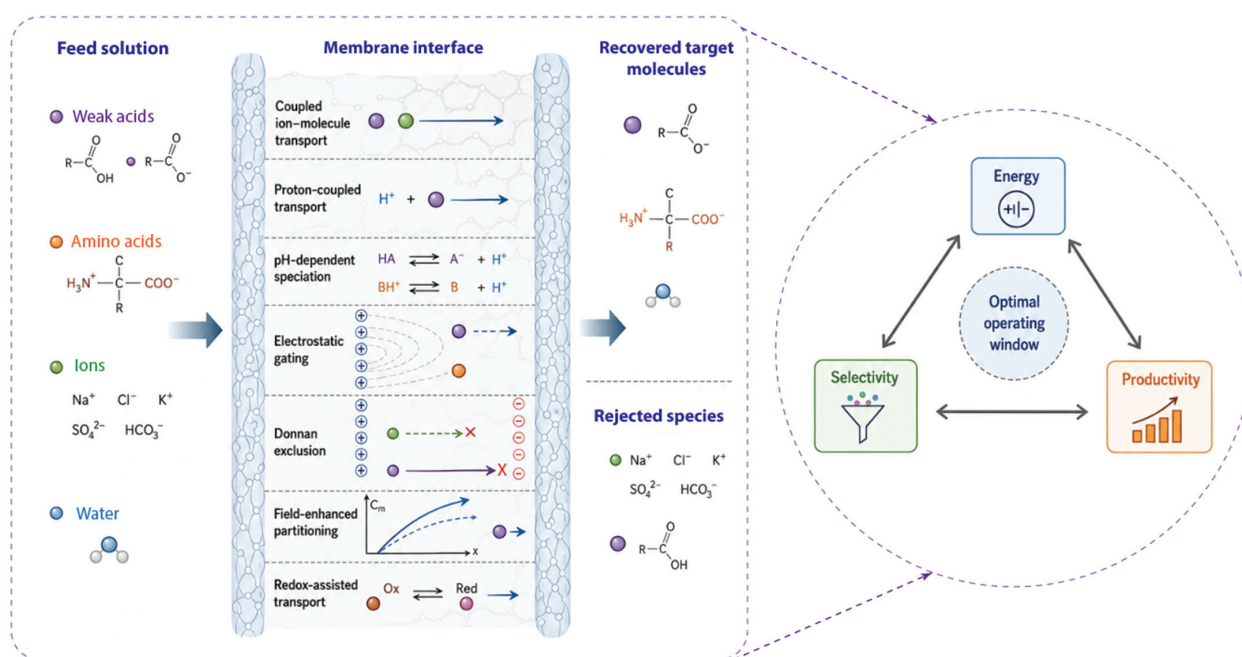


Figure 2. The physics and thermodynamics of electrified membrane interfaces. **(Left)** Active, speciation-controlled transport mechanisms—including electrostatic gating, redox affinity, and Donnan exclusion—that bypass passive size-exclusion. **(Right)** The inescapable macro-scale thermodynamic nexus, illustrating the strict operational tradeoff among interfacial selectivity, volumetric productivity, and energy consumption.

2.1. Coupled Ion–Molecule Transport Dynamics

Electromigration is conventionally defined as the movement of fixed-charge species under an electric field. However, the transport of biological target molecules is vastly more complex because these species exist in multiple protonation states that continuously adapt to their local electrochemical environment [23–26]. Organic acids, amino acids, and vital fermentation intermediates exhibit dynamic speciation, meaning their effective charge, hydrodynamic volume, and mobility fluctuate dynamically during the separation process. Transport physics cannot, therefore, be decoupled from proton transport, localized acid–base equilibria, or concentration polarization phenomena. Weak aliphatic organic acids (e.g., lactic, succinic, and acetic acids) perfectly illustrate this complexity.

These compounds continuously transition between neutral and dissociated anionic states dictated by their acid dissociation constants (pKa) and the localized pH [12,27–29]. Because the electric field solely acts upon the charged fraction, local pH gradients continuously alter the mass of molecules susceptible to electromigration. The electric field thereby drives separation through a dual mechanism: enforcing directional motion while simultaneously altering the chemical identity of the permeant through field-induced water dissociation and localized proton flux.

To quantitatively describe this coupled behavior, classical transport theories must be modified. In standard desalination, ionic flux across an ion-exchange membrane is modeled using the classical Nernst–Planck equation, which sums diffusive, electromigrative, and convective transport for species with a static valence (z_i):

$$J_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla \phi + c_i v$$

where J_i is the molar flux, D_i is the diffusion coefficient, c_i is the concentration, F is the Faraday constant, R is the universal gas constant, T is absolute temperature, ϕ is the electrical potential, and v is the convective fluid velocity. However, for weak organic acids,

this static formulation collapses because the effective valence is a variable function of the localized boundary-layer pH. The effective anionic flux must therefore be weighted by the degree of dissociation (α), governed by the Henderson–Hasselbalch speciation relationship:

$$J_{\text{organic}} = -\alpha D_{\text{app}} \nabla c_{\text{total}} - \frac{\alpha(-1)F}{RT} D_{\text{app}} C_{\text{total}} \nabla \phi + c_{\text{total}} v$$

$$\alpha = \frac{1}{1 + 10^{(pK_a - pH_{\text{local}})}}$$

Here, pH_{local} is the dynamic pH at the membrane–solution interface, which deviates significantly from the bulk fluid due to concentration polarization and water dissociation. This mathematical coupling demonstrates that electromigrative flux is fundamentally governed by localized proton gradients rather than bulk concentrations alone. Crucially, these classical transport frameworks assume ideal, dilute electrolyte behavior and static membrane morphology. In industrial bioseparations, these theoretical assumptions are regularly challenged by multicomponent ion competition, non-ideal activity coefficients, osmotic membrane swelling, concentration polarization, and organic fouling, which collectively alter effective ion mobility and boundary-layer equilibria over extended operation.

Charge regulation further dictates transport dynamics. Unlike simple inorganic electrolytes (Na^+ , Cl^-) possessing fixed valences, biocolloids and nitrogenous biochemicals exhibit variable surface charge distributions. Amino acids, for instance, transition between cationic, anionic, and zwitterionic states depending on the proximity of the local pH to their isoelectric points (pI) [30]. At the isoelectric point, the net electrophoretic mobility plummets to zero despite a strong external electric field, rendering the molecule temporarily immune to electromigration but highly susceptible to passive diffusion or localized precipitation. Consequently, separation is governed by manipulating the thermodynamic minimum of the molecule's charge state rather than exploiting intrinsic molecular size.

The prevailing literature frequently attempts to model bio-based electromigration using classical Nernst–Planck frameworks developed for seawater desalination, treating organic target molecules as if they possess fixed charges [31–33]. This is a fundamental thermodynamic flaw. The dominant limitation in predicting and scaling bio-separations is the dynamic coupling between molecular speciation and the localized proton flux. Future theoretical frameworks and digital twins must abandon static-charge assumptions and co-engineer transport algorithms that integrate real-time reactive-transport coupling, treating bioseparation as a multicomponent electrochemical reaction rather than a simple migration process.

2.2. Interfacial Selectivity Mechanisms

The distinguishing capability of electrified membranes is their ability to selectively regulate molecular transport at the angstrom scale. Precise separation is primarily an interfacial phenomenon rather than a function of bulk membrane morphology [34–36]. Donnan-mediated exclusion is the foundational mechanism, where fixed charges within the membrane matrix establish steep electrostatic potential gradients at the solution interface [37,38]. In equilibrium electrolyte systems, the Donnan potential (ψ_{Donnan}) across the membrane interface is defined by the ratio of ion activities:

$$\psi_{\text{Donnan}} = \frac{RT}{z_i F} \ln \left(\frac{a_{i, \text{membrane}}}{a_{i, \text{solution}}} \right)$$

While well-understood for bulk desalination, Donnan effects in bioseparations are highly dynamic. Because the charge of the target organic molecule shifts with local speciation, Donnan exclusion evolves continuously throughout the separation timeline, coupling

membrane charge density directly with boundary-layer solution chemistry. Electrostatic gating represents the programmable evolution of this principle. Rather than relying on passive, permanently charged polymer networks, stimuli-responsive interfaces actively regulate molecular accessibility via externally modulated electric potentials [39,40].

Modulating the applied voltage alters the thickness and charge density of the electrical double layer (EDL) at the membrane surface, effectively acting as an energetic gate that permits or restricts entry based on molecular dipole moments and charge distributions. Field-enhanced partitioning further disrupts traditional separation thermodynamics. In passive separations, partitioning depends strictly on the chemical affinity between the solute and the polymer matrix. Electrified interfaces, however, artificially modify these equilibria by altering the dielectric environment [41,42]. Polarizable biological molecules experience field-induced orientation and altered hydration energies, creating transport pathways that defy standard equilibrium partition coefficients.

Additionally, redox-assisted transport systems integrate faradaic reactions directly at the interface [43,44]. By reversibly oxidizing or reducing target species during transit, these interfaces transiently convert molecules into highly mobile intermediates before regenerating the native compound downstream, blurring the strict boundary between electrochemical synthesis and molecular purification. Current material science studies overwhelmingly focus on optimizing bulk membrane composition—synthesizing novel polymers or casting complex nanocomposites. However, molecular discrimination occurs almost entirely within the nanoscopic electrical double layer at the interface. Treating the membrane merely as a static conductive barrier is a missed opportunity. Future material design must pivot toward engineering programmable, electro-responsive interfaces capable of dynamically shifting their local dielectric environments and electrostatic gating thresholds to match the fluctuating speciation of complex biological broths.

2.3. The Interfacial Tradeoff: Selectivity, Mass Transfer, and Energy Barriers

A pervasive and flawed assumption in membrane engineering is that maximizing interfacial selectivity unilaterally improves system performance. In reality, electro-driven bioseparations are strictly governed by an inescapable micro-scale thermodynamic tradeoff linking molecular discrimination, mass transfer (productivity), and specific energy consumption ($\text{kWh/kg}_{\text{product}}$) [45,46]. To maintain terminology consistency across this review, this phenomenon is defined specifically as the interfacial transport tradeoff, distinguishing it from the macro-scale techno-economic and system-level scaling constraints discussed in Section 6.

High interfacial selectivity demands that non-target molecules face steep activation energy barriers ($\Delta G^\ddagger$) preventing their transport. However, establishing these high energy barriers—whether through intense electrostatic exclusion, rigid sub-nanometer confinement, or profound hydration-shell stripping—inevitably impedes the mass transfer of the target molecule as well. Increasing molecular discrimination therefore exponentially decreases flux. Compensating for this reduced productivity typically requires elevating the applied voltage to forcefully drive the target molecule over the barrier [11]. This brute-force thermodynamic compensation severely inflates the specific energy consumption, rapidly eroding the economic viability of the process when benchmarked against traditional thermal separations.

Conversely, attempting to maximize productivity by applying excessive current densities fundamentally degrades selectivity. High driving forces accelerate concentration polarization, disrupt the electrical double layer, and trigger localized water splitting. Under these conditions, the electrical energy is consumed by parasitic proton/hydroxide transport and the migration of competing inorganic salts, rather than the target biochemical [47,48].

Consequently, system purity crashes, and the energetic efficiency of the target separation collapses. Selectivity and productivity are inextricably bound within the same transport energy landscape; adjusting the electrical driving force alters the barrier heights for all species simultaneously.

The bioseparation literature is saturated with studies reporting either exceptional interfacial selectivity or unprecedented molecular flux as isolated, independent breakthroughs [49–52]. Reporting these metrics without rigorously quantifying the associated specific energy penalty ($\text{kWh/kg}_{\text{product}}$) obscures the true thermodynamic cost of the separation. Future innovations will not emerge from empirically pushing a single metric to its extreme, but from rationally designing nanoconfined interfaces that fundamentally decouple this tradeoff—flattening the activation energy curve for target bio-molecules while maintaining insurmountable thermodynamic barriers for structural analogues.

Table 1 demonstrates that electro-selective transport in bio-based chemical recovery is not governed by a singular physical mechanism, but by the dynamic coupling of electrochemical potential, molecular speciation, interfacial partitioning, and multicomponent interactions. Consequently, future membrane design must prioritize the engineering of programmable, responsive transport environments rather than merely optimizing bulk ionic conductivity or static membrane charge density.

Table 2. Advanced electro-selective transport mechanisms for organic molecules.

Transport Mechanism	Thermodynamic Driving Force	Representative Target Molecules	Quantitative Indicators and Energetic Implications	Critical Engineering Perspective and Operational Limitations	Refs.
Field-Induced Electromigration	Electrostatic potential gradient ($\nabla\phi$) acting upon ionized species.	Aliphatic organic acid anions (lactate, acetate, succinate).	• SEC: 0.5–2.5 $\text{kWh/kg}_{\text{product}}$ • Operating Window: 1.0–3.0 V/cell • Efficiency: Exceeds 90% current efficiency (η) in clean, ionic solutions.	• Limitation: In dilute biological broths, SEC increases sharply due to parasitic current consumption by background mobile salts (K^+, Cl^-). • Engineering Trade-off: Recovery is strictly limited to the ionized fraction (α), requiring precise boundary-layer pH regulation alongside voltage control.	[53–56]
Proton-Coupled Transport	Superposition of localized proton flux and applied electric fields.	Weak organic acids, volatile fatty acids (VFAs), pH-sensitive metabolites.	• SEC: 1.5–4.5 $\text{kWh/kg}_{\text{product}}$ • Operating Window: >1.2 V (exceeding theoretical water splitting threshold). • Efficiency: Replaces 100% of external acid/base chemical dosing.	• Limitation: Field-induced water dissociation at bipolar junctions incurs an inherent overpotential penalty. • Engineering Trade-off: Separation is governed by Henderson–Hasselbalch equilibria; modulating interfacial proton flux is frequently more effective than increasing electric field strength.	[23,57,58]

Table 2. Cont.

Transport Mechanism	Thermodynamic Driving Force	Representative Target Molecules	Quantitative Indicators and Energetic Implications	Critical Engineering Perspective and Operational Limitations	Refs.
Dynamic Donnan Exclusion	Electrostatic potential differentials established by fixed membrane charge densities.	Charged organic acids, multifunctional ionic biopolymers.	• SEC: 0.3–1.8 kWh/kg_{product} • Operating Window: 0.5–2.0 V/cell • Efficiency: Enhances co-ion rejection (>98%) without requiring elevated voltages.	• Limitation: Bulk membrane ion-exchange capacity (IEC) alone does not predict performance in complex matrices. • Engineering Trade-off: Because target molecule speciation evolves during transit, the effective Donnan potential is continuously altered by boundary-layer ionic strength and pH shifts.	[59,60]
Electrostatic Surface Gating	Voltage-modulated polarization of the interfacial electrical double layer (EDL).	Zwitterionic compounds (amino acids), small organic ions, selective metabolites.	• SEC: 0.8–3.0 kWh/kg_{product} • Operating Window: Pulsed or variable potential (<1.5 V). • Efficiency: Increases initial product purity by 15–30%, reducing downstream polishing demands.	• Limitation: Requires responsive electrode/membrane architectures and real-time voltage modulation hardware. • Engineering Trade-off: Transitions separation from passive size exclusion to active gating, enabling on-the-fly selectivity adjustments responsive to shifting fermentation pH.	[32]
Field-Enhanced Partitioning	Electric-field-induced modification of local dielectric constants and hydration energies.	Polar organic molecules, partially ionized intermediates, phenolic compounds.	• SEC: 1.0–3.5 kWh/kg_{product} • Operating Window: High field gradients (>10⁶ V/m across interface). • Efficiency: Modifies solute partition coefficients (K) by 2–5 × compared to passive diffusion.	• Limitation: High interfacial field gradients can accelerate localized membrane scaling and organic deposition. • Engineering Trade-off: Transport is governed by altered dielectric environments rather than Nernst–Planck mobility, offering a viable pathway for separating structural isomers.	[61–63]
Affinity-Assisted Electrotransport	Synergistic coupling of electromigration with specific chemical affinities (H-bonding, π - π stacking).	Aromatic acids, targeted phenolics, specialized high-value biochemicals.	• SEC: 1.2–4.0 kWh/kg_{product} • Operating Window: Low voltage (0.5–1.5 V/cell), minimizing Ohmic heating. • Efficiency: Enhances selectivity factors ($\alpha_{A/B}$) by an order of magnitude over size exclusion.	• Limitation: Periodic membrane regeneration or desorption cycles introduce intermittent energetic and chemical costs. • Engineering Trade-off: Requires embedding specific functional ligands directly into conductive polymer matrices without compromising mechanical stability or electrical conductivity.	[1,12,64]

Table 2. Cont.

Transport Mechanism	Thermodynamic Driving Force	Representative Target Molecules	Quantitative Indicators and Energetic Implications	Critical Engineering Perspective and Operational Limitations	Refs.
Redox-Assisted Transport	Reversible faradaic oxidation/reduction altering molecular charge states during transit.	Electroactive organics, quinones, targeted biomass-derived platform chemicals.	• SEC: 2.5–6.0 kWh/kg_{product} (includes Faradaic electron transfer energy). • Operating Window: System-specific redox potentials (E°). • Efficiency: Combines separation and molecular conversion into a single unit operation.	• Limitation: Demands continuous electrical energy to drive Faradaic cycling, and electrode passivation can degrade long-term performance. • Engineering Trade-off: Represents a process intensification strategy that blurs the thermodynamic boundary between chemical synthesis and downstream purification.	[65–68]
Nano-Confined Electrokinetics	Electric-field modulation within sub-nanometer, sterically restricted channels.	Low-molecular-weight metabolites, precise amino acid fractionation.	• SEC: 1.5–5.0 kWh/kg_{product} • Operating Window: Sub-nanometer pores (<1.0 nm). • Efficiency: Minimizes parasitic water transport (electro-osmotic drag) and co-ion leakage.	• Limitation: Fabrication of uniform, defect-free sub-nanometer channels currently presents severe CapEx and scalability constraints. • Engineering Trade-off: Forces partial solute dehydration during transit, enabling simultaneous steric and electrostatic discrimination for molecules with identical charge-to-mass ratios.	[69–71]

3. Electrified Membrane Platforms for Bio-Based Chemical Recovery

The functional evolution of electro-driven membrane technologies reflects a broader transition from bulk ion removal to precision molecular recovery. Conventional literature classifications typically organize these technologies according to hardware architecture—drawing rigid boundaries between electrodialysis, bipolar membranes, or capacitive systems [72,73]. While valuable from a mechanical engineering perspective, this architectural framework fails to address the underlying thermodynamic objective of modern biorefineries: the selective extraction of chemically diverse target molecules from highly complex, fluctuating aqueous environments.

Unlike seawater desalination, which primarily targets the bulk removal of predictable, permanently charged inorganic ions, bio-based separations must overcome dilute product titers, dynamic molecular speciation, competitive structural analogues, and continuously evolving fermentation matrices. The efficacy of an electrified platform therefore depends less on its cell configuration than on its ability to manipulate the interfacial transport physics established in Section 2. Each platform must be evaluated based on how it integrates localized pH regulation, electrostatic discrimination, and electrochemical driving forces to achieve molecular selectivity.

To provide a rigorous, systematic comparison, the platforms in this section are classified according to their primary thermodynamic driving force and their functional integration role within the biorefinery flowsheet: (1) electromigration-driven fractionation, (2) water-dissociation-driven speciation control, (3) double-layer capacitive electrosorption, and (4) bio-catalytically driven extraction. Consequently, as conceptualized in Figure 3, electro-driven membrane systems (EDMS) must be reclassified according to their functional role within the bioprocess—ranging from speciation-controlled fractionation to in situ

bioreactor integration. Their comparative operational niches, target compound classes, inherent thermodynamic limitations, and scaling metrics are synthesized in Table 3.

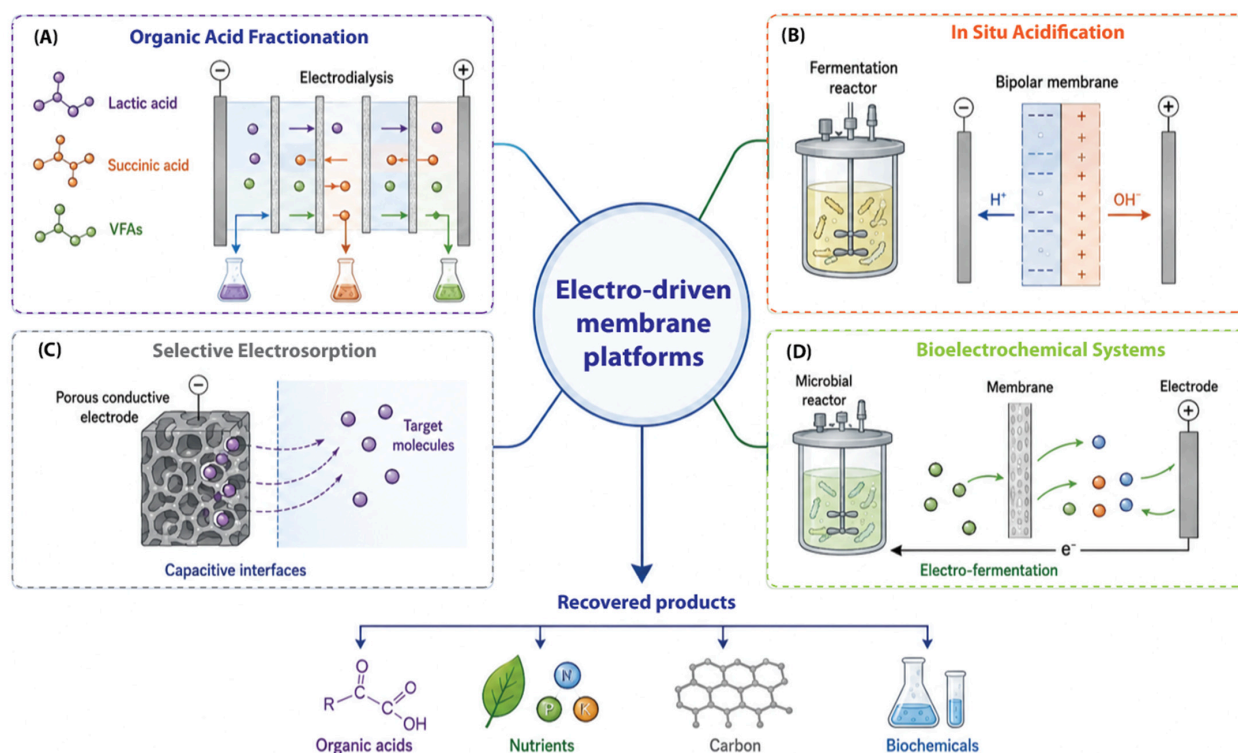


Figure 3. Functional taxonomy and operational niches of electrified bioseparation architectures. The platforms exploit distinct thermodynamic mechanisms to achieve targeted molecular recovery: (A) speciation-controlled electrodialytic fractionation of homologous organic acids; (B) bipolar membrane-driven in situ acidification and pH buffering; (C) reversible capacitive electrosorption at porous interfaces; and (D) coupled bioelectrochemical extraction. Together, these systems establish the foundation for extracting platform biochemicals and nutrients directly from complex fermentation loops.

3.1. Organic Acid Fractionation via Electrodialysis: From Desalting to Speciation-Controlled Extraction

Electrodialysis (ED) has rapidly emerged as the foundational platform for recovering bio-based aliphatic organic acids. Its primary industrial value lies in displacing the massive chemical and thermal penalties of conventional purification routes; extracting organic acids directly via electromigration circumvents the latent heat of vaporization inherent to distillation, and eliminates the stoichiometric generation of secondary solid wastes (e.g., gypsum) associated with classical calcium-precipitation methods [55,74–76]. However, its application in contemporary biorefining extends far beyond simple ion migration. The true utility of ED is its capacity for speciation-controlled fractionation, wherein selective transport is dictated by the dynamic interplay between molecular ionization and localized electrochemical gradients. The recovery of platform chemicals such as lactic, succinic, and mixed volatile fatty acids (VFAs) is fundamentally constrained by the realities of microbial fermentation [26,77,78].

These target molecules are typically generated in complex broths where substantial fractions remain partially protonated. Because exclusively ionized species undergo electromigration, separation efficiency is dictated by the precise equilibrium between protonated and dissociated forms. To maintain terminology consistency across literature comparisons, it is necessary to distinguish between bulk removal (non-selective depletion of total dissolved solids), recovery (mass yield of the target compound transferred to the concentrate

stream), enrichment (the increase in target-to-impurity ratio), and purification (the final mass fraction of the target chemical). State-of-the-art modeling integrating dielectric exclusion and Donnan-steric pore frameworks reveals that up to 99% of target acid rejection and selection occurs strictly at the angstrom-scale membrane interface, governed by local dielectric constants rather than bulk diffusion [79].

Translating this thermodynamic reality to complex agro-industrial matrices (e.g., acid whey, corn steep water, or anaerobic digestate) requires sophisticated process intensification. The literature demonstrates that deploying unmodified ED on raw fermentates yields sluggish transport and severe specific energy consumption due to the parasitic current drawn by competing inorganic background salts (e.g., chlorides, phosphates) [80,81]. However, when integrated holistically—such as coupling reverse osmosis or nanofiltration pre-concentration with ED—the specific energy consumption (SEC) for extracting acids like acetic or lactic acid can be suppressed to highly competitive margins of 0.37 to 1.0 kWh/kg_{product} [80,82,83]. This energetic footprint is a fraction of the thermal energy required for multi-stage evaporation, fundamentally validating the economic viability of the electrified pathway.

Furthermore, the selective extraction of VFAs highlights the critical distinction between partition selectivity and mobility selectivity. Recent systematic evaluations demonstrate that in multicomponent broths, VFA transport is severely depressed by the presence of competing counterions possessing higher membrane affinities [23]. To achieve true chemical-grade purity, ED must therefore be paired with complementary driving forces. For example, hybridizing ED with hydrophobic membrane contactors ensures that extracted VFAs are selectively stripped from co-migrating inorganic nutrients (yielding >94% VFA purity with <2% nutrient contamination), effectively fractionating the stream into discrete bio-based chemical and fertilizer precursor lines [84].

Beyond downstream fractionation, the ultimate architectural advantage of ED is its capacity for continuous, in situ product recovery directly coupled to live bioreactors. By continuously extracting inhibitory organic acids as they are metabolically synthesized, extractive electrodialysis alleviates end-product toxicity, stabilizing bioreactor pH without the need for constant alkaline dosing [85,86]. Under optimized current densities, this configuration shifts the bioprocess from batch limitations to a continuous manufacturing paradigm, significantly amplifying total volumetric productivity.

Engineering Trade-offs and Operational Constraints: Current literature predominantly optimizes ED for bio-based recovery by screening commercial desalination membranes or varying bulk current densities, treating the electrodialysis stack as a passive, isolated downstream unit. This approach encounters a severe operational limitation: the dynamic thermodynamic coupling between competitive multicomponent transport and the fluctuating rheology and speciation of live fermentation broths. To overcome this limitation, future ED architectures must transition from static operational set-points toward adaptive systems. Implementing pulsed electric fields and machine-learning-guided real-time voltage modulation can dynamically align the electrical driving force with the shifting isoelectric points and acid dissociation constants of the evolving bioreactor matrix, mitigating membrane fouling while optimizing current efficiency.

3.2. In Situ Acidification and pH Swing Separation Through Bipolar Membranes

Bipolar membrane (BPM) systems represent a highly effective electrochemical intervention in modern bioseparations because they decouple pH regulation from exogenous chemical dosing. Conventional biorefining requires massive volumetric additions of external acids and bases to induce product precipitation or shift metabolic pathways, inadvertently inflating downstream salinity, generating stoichiometric solid waste, and

complicating final purification [87–89]. Bipolar membranes circumvent this thermodynamic bottleneck by electrochemically forcing the dissociation of water into discrete proton (H^+) and hydroxide (OH^-) fluxes precisely at the membrane interface. However, within the context of bio-based chemical recovery, the utility of BPMs extends far beyond the bulk generation of commoditized acids and bases.

Their primary value lies in programmable pH-swing extraction. Because the transport and adsorption of biological molecules (e.g., weak organic acids, zwitterionic amino acids, dissolved ammonia) are rigidly governed by local acid-base equilibria, the localized proton flux from a BPM functions as a dynamic speciation switch. By precisely tuning the electrical current, BPMs can drive a target molecule across its isoelectric point or acid dissociation constant (pK_a) in transit. This enables, for example, the selective concentration of weak carboxylic acids (e.g., itaconic acid) with extraction efficiencies fivefold higher than conventional membrane capacitive deionization by manipulating Pourbaix-guided speciation states within the electrical double layer [90]. Similarly, targeted pH modulation via BPMs seamlessly drives dissolved ammonium (NH_4^+) into volatile ammonia (NH_3) for subsequent membrane stripping without caustic chemical dosing [91].

Translating this capability to complex, highly concentrated fermentation matrices exposes severe physical and material limitations. The generation of high-purity, highly concentrated bio-acids or base byproducts is aggressively hindered by proton leakage—the parasitic back-migration of H^+ through the adjacent anion exchange membranes, which decimates current efficiency at elevated acid concentrations [92]. While conventional pilot-scale BPM configurations efficiently process 2.0–3.0 M saline feeds to yield moderate 0.8–2.0 M acid/base concentrations at specific energy consumptions (SEC) of 1.02 to 2.18 kWh/kg [93,94], surpassing these thermodynamic limits requires aggressive process intensification.

Recent advances demonstrate that replacing standard membranes with proton-blocking polymer inclusion membranes suppresses H^+ leakage, enabling peak acid recoveries of >2.35 M at near-perfect anion selectivities [95]. Furthermore, transition from single-pass architectures to multistage-batch volumetric manipulations has successfully driven base concentrations to an unprecedented 3.40 M [96]. Despite these material advances, the energetic footprint of BPM water dissociation remains a vulnerability, particularly when treating raw industrial broths where high chemical oxygen demand (COD) severely inflates Ohmic resistance and exacerbates energy consumption [97].

Consequently, the frontier of BPM engineering involves fundamentally altering the electrochemical reaction itself. Disruptive approaches, such as redox-mediated bipolar electrodialysis, substitute the energy-intensive water-splitting reaction with sustainable ferri-/ferrocyanide faradaic redox couples. This mechanistic substitution allows the cell to operate at a mere 1.2 V, successfully suppressing the specific energy consumption to 0.55 kWh/kg—a >50% reduction in OpEx compared to conventional BPM water dissociation [98].

Engineering Trade-offs and Operational Constraints: The prevailing literature frequently evaluates BPM innovation based on the maximum molarity of acid or base generated from synthetic brines [89,90,99]. For bio-based separations, however, targeting extreme molarity can be counterproductive. In live fermentations or sensitive enzymatic broths, extreme localized pH gradients can denature proteins, promote membrane scaling, and induce cellular toxicity. Consequently, BPM research for biorefinery integration should prioritize high-precision, low-voltage localized buffering over bulk concentration. Developing automated, pulsed-current protocols that restrict water dissociation strictly to the thermodynamic minimum required to sustain a target interfacial pH will be essential for integrating BPMs directly into continuous, live biomanufacturing loops.

3.3. Selective Electrosorption Through Capacitive Interfaces

Capacitive electro-driven systems introduce a fundamentally distinct thermodynamic pathway for bio-based recovery: reversible electrostatic sequestration rather than continuous trans-membrane migration [100,101]. While conventional electrodialysis (ED) becomes prohibitively energy-intensive when processing highly dilute streams—as the depletion of charge carriers triggers severe Ohmic resistance—capacitive deionization (CDI) excels in low-concentration regimes. By applying an electrical potential across porous conductive interfaces, target species are transiently immobilized within the electrical double layer (EDL) and subsequently concentrated via potential reversal. This operational decoupling of the adsorption and desorption phases enables immense volumetric reduction without the latent heat penalties of thermal evaporation.

However, the application of CDI in biorefineries extends far beyond the non-selective desalting of wastewater. Advanced capacitive platforms now integrate structural nanoconfinement, specific chemical affinities, and faradaic reactions to achieve exquisite molecular discrimination in highly competitive matrices. The recovery of critical biogenic nutrients (e.g., phosphate and ammonium) exemplifies this transition from passive EDL formation to programmable interfacial affinity. In complex anaerobic digestates, purely electrostatic carbon electrodes exhibit notoriously poor selectivity due to aggressive competition from abundant co-ions (e.g., chlorides, sulfates).

To circumvent this, state-of-the-art capacitive interfaces are increasingly engineered with specific binding motifs. For example, modifying membrane capacitive deionization (MCDI) electrodes with covalent organic frameworks (COFs) leverages intense hydrogen-bonding to elevate phosphate selectivity up to sevenfold over competing anions [102]. Similarly, the incorporation of redox-active transition metals—such as goethite (α -FeOOH) or layered double hydroxides (LDH) within biochar matrices—facilitates reversible inner-sphere Fe–O–P complexation [103,104]. These sophisticated architectures achieve remarkable phosphate enrichment factors exceeding 11- to 15-fold directly from raw digestate permeate.

Crucially, the specific energy consumption (SEC) of these advanced capacitive separations ranges from 1.89 to 9.07 kWh/kg P for phosphate [25,103–105], and 0.45 to 3.03 kWh/kg N for ammonium [106–108]—energetic footprints that decisively undercut conventional massive chemical precipitation and thermal ammonia stripping processes. For the recovery of medium- and short-chain volatile fatty acids (VFAs), capacitive platforms offer an alternative to the severe proton-leakage issues inherent to bipolar membrane systems. By manipulating the localized pH gradients that naturally occur adjacent to polarized electrodes, systems can drive the in situ protonation and desorption of carboxylates. Electrosorbed VFA anions migrating toward the anode can be continuously harvested by converting them into their neutral acid form within an acidic boundary layer, achieving >50% selective recovery of target molecules like caproate and butyrate [24,109].

To overcome the finite adsorption capacity of static electrodes, fluidic architectures such as flow-electrode CDI (FCDI) have emerged. By circulating conductive carbon slurries (often enhanced with highly mobile 2D materials like MXenes or graphene) through the cell, FCDI systems provide a virtually infinite sink for ion accumulation [107,108]. Furthermore, these flowable electrodes act as dynamic chemical reactors; for instance, the continuous electrosorption of ammonium and phosphate into a magnesium-enriched flow-electrode inherently drives the localized precipitation of high-purity struvite nanowires, simultaneously separating the target ions and synthesizing a valuable slow-release fertilizer [110].

Engineering Trade-offs and Operational Constraints: Despite promising specific energy metrics, the capacitive recovery of organic acids faces a severe material challenge regarding anodic durability. Applying potentials exceeding 1.2 V to achieve high VFA

adsorption capacity frequently induces Faradaic oxidation of the carbon electrode matrix [24,100]. Over extended cycling (>1000 cycles), specific surface area and pore volume can degrade significantly due to carbon corrosion and Kolbe-type oxidation of target carboxylates. Furthermore, in raw fermentation broths, hierarchical mesopores are susceptible to fouling by extracellular polymeric substances (EPS) and proteins. Mitigating these limitations requires transitioning from bare activated carbons toward conductive, anti-fouling protective coatings and robust intercalation materials (such as transition metal carbides) that operate via pseudo-capacitance, thereby minimizing reliance on vulnerable carbon oxidation chemistry.

3.4. Bioelectrochemical Membrane Systems: Integrating Fermentation and Extraction

A major conceptual advancement in electro-driven bioseparations is the development of bioelectrochemical membrane systems (BES). Traditional bioprocessing isolates upstream biological conversion from downstream purification, which can impose batch limitations due to product toxicity and necessitate energy-intensive secondary unit operations. BES architectures address this separation by utilizing electroactive microorganisms that naturally exchange electrons with conductive interfaces, establishing a continuous, closed-loop feedback between microbial metabolism and electro-driven molecular transport [111].

In a BES architecture, the membrane functions not only as a separation barrier but also as an active regulator of the biological microenvironment. By continuously extracting inhibitory end-products and toxic metabolites as they are synthesized, the membrane alleviates localized product inhibition. This dynamic extraction enables higher volumetric productivities and prolonged continuous fermentation cycles compared to conventional batch reactors [112,113].

The most mature application of BES lies in the extraction and valorization of nutrients from highly concentrated, complex organic effluents (e.g., dairy manure, slaughterhouse wastewater, coal-chemical effluents). Traditional ammonia stripping requires massive bulk chemical dosing to raise the pH above 10.0, followed by energy-intensive thermal stripping. BES architectures, such as Microbial Electrolysis Cells (MEC), circumvent this entirely. By oxidizing the complex organic matter (chemical oxygen demand, COD) at the bio-anode, the system generates an internal electrical current that drives ammonium (NH_4^+) across a cation exchange membrane toward the cathode.

Simultaneously, localized cathodic proton reduction naturally elevates the boundary-layer pH, driving the equilibrium shift from dissolved NH_4^+ to volatile ammonia (NH_3) without a single drop of exogenous caustic reagent [114,115]. When optimized with hydrophobic gas-permeable membranes, these systems report extraordinary recovery rates of up to $55 \text{ gN-NH}_4^+ / \text{m}^2 / \text{d}$, extracting 97% of the total nitrogen directly as a concentrated, chemical-grade ammonium sulfate fertilizer [116].

Crucially, the performance of BES is governed by a strict thermodynamic tradeoff between biological kinetics and transport energy. At low influent concentrations ($\sim 0.5 \text{ g/L NH}_4^+$), the mass transfer resistance across the membrane dominates, and the specific energy consumption for extraction hovers at a relatively high 3.6 kWh/kg N [117]. However, as the localized substrate concentration increases (up to 1.5 g/L), the biofilm metabolic activity surges, amplifying the current density to 3.9 A/m^2 . This bio-catalytically driven current physically accelerates the electromigration of the target molecule, dropping the specific extraction energy to 2.1 kWh/kg N while simultaneously degrading 80–95% of the influent COD [117–119].

Beyond nitrogen, cutting-edge BES configurations have successfully integrated in situ crystallization directly into the bio-reactor. For example, “electrochemical anaerobic membrane bioreactors” utilizing sacrificial magnesium anodes not only recover carbon

(as high-purity >93% methane) but also continuously release Mg^{2+} ions. These ions react with electro-migrated phosphate and ammonium at the cathode to precipitate high-purity struvite [120]. Remarkably, the continuous generation of Mg^{2+} alters the physicochemical properties of the sludge, actively unblocking the membrane cake layer and achieving 95% anti-fouling efficiency. Similarly, three-chamber bio-electrodialysis systems have demonstrated >650% enrichment ratios for phosphate recovery from dilute streams, driven purely by the microbially generated voltage [121].

Engineering Trade-offs and Operational Constraints: Despite the elegant theoretical integration of BES, the literature suffers from a fatal scaling paradox. Studies continually report high extraction efficiencies using synthetic, highly buffered, or perfectly balanced (C:N ratio) feed streams. In reality, scaling these systems in raw industrial broths frequently exposes severe limitations: the current density generated by the bio-anode is rarely sufficient to drive the necessary flux of the target molecule without massive external voltage supplementation. For example, treating low-strength municipal wastewater required 152 kWh/kg N removed—an energy penalty that destroys economic viability [115]. Advancing BES toward commercial deployment requires optimizing bio-anode surface area and current density, while aligning the stoichiometric alkalinity and carbon-to-nitrogen ratios of real feedstocks with the electrochemical transport demands of the membrane stack.

To prevent misleading comparisons across different stages of maturity, reported performance indicators (such as SEC and recovery efficiency) must be interpreted strictly within their designated feed categories; values derived from idealized synthetic solutions or model broths represent baseline thermodynamic potential, whereas metrics from raw industrial digestates and effluents reflect authentic operational constraints.

Table 3. Functional Performance and Techno-Economic Limitations of Electrified Bioseparation Platforms.

Functional Platform	Target Compound Class	Typical Membrane and Electrode Materials	Operating Voltage and Current Density	Specific Energy Consumption (SEC) and Recovery	Operating pH Window and Feed Type	TRL	Rate-Limiting Thermodynamic and Engineering Constraints
Electrodialysis (ED) (<i>Speciation-Controlled Fractionation</i>)	Aliphatic organic acids (lactic, succinic, VFAs), charged nitrogenous compounds [26,55,75,77,84,91,92,95].	Membranes: Homogeneous/heterogeneous AEMs and CEMs (e.g., polystyrene-DVB, PVDF matrices). Electrodes: Ti/Pt or Dimensionally Stable Anodes (DSA).	Voltage: 1.0–2.5 V/cell Current Density: 10–50 mA/cm²	SEC: 0.37–1.5 kWh/kg_{product} Recovery: 80–95% (in pre-treated broths).	pH Window: 4.0–7.5 (governed by target pKa). Feed Type: Raw fermentation broths, acid whey, anaerobic digestates.	6–8	Parasitic Current: SEC increases exponentially in raw broths due to preferential electromigration of highly mobile background salts (K⁺, Cl[−]) over bulky organic anions. Mitigation: Requires NF/RO pre-concentration or in situ crystallization coupling.
Bipolar Membrane Systems (EDBM/BPMED) (<i>In Situ pH-Swing Extraction</i>)	Weak organic acids, aqueous ammonia, pH-sensitive biopolymers [90,91,95,122,123].	Membranes: Bipolar membranes with catalyst interlayers (e.g., Ti₃C₂T_x, graphene oxide doped), paired with standard AEMs/CEMs. Electrodes: Ti/Pt or IrO₂-coated Ti.	Voltage: 1.5–3.5 V/cell (must exceed 1.23 V thermodynamic water-splitting threshold). Current Density: 20–60 mA/cm²	SEC: 1.02–2.5 kWh/kg_{product} Recovery: 75–90%	pH Window: 1.0–14.0 (generates localized acid/base gradients). Feed Type: Concentrated bioreactor effluents, high-COD saline brines.	5–7	Proton Leakage: Producing acid/base concentrations exceeding 2.0 M triggers severe H⁺ back-migration across the anion exchange layer, reducing current efficiency (< 60%). Mitigation: Requires proton-blocking polymer inclusion membranes or redox-mediated couples.
Capacitive Interfaces (MCDI/FCDI) (<i>Selective Electrosorption</i>)	Dilute nutrients (NH ₄ ⁺ , PO ₄ ^{3−}), volatile fatty acids, low-concentration metabolites [24,100,106–109].	Membranes: Thin protective AEMs/CEMs. Electrodes: Porous activated carbon, carbon aerogels, COF-modified biochar, or flowing carbon slurries (1–5 wt%).	Voltage: 0.8–1.2 V (strictly below carbon oxidation threshold). Current Density: 2–15 mA/cm²	SEC: - Nutrients: 0.45–3.0 kWh/kg N - VFAs: 1.8–4.5 kWh/kg Recovery: 65–85%	pH Window: 5.0–8.5 (constrained by carbon electrode stability). Feed Type: Municipal wastewater, highly dilute secondary fermentation effluents.	4–5	Anodic Oxidation: Operating carbonaceous electrodes above 1.2 V triggers irreversible Faradaic oxidation and pore collapse. Mitigation: Requires transitioning to flow-electrode architectures (FCDI) or pseudo-capacitive transition metal coatings to bypass static adsorption exhaustion.

Table 3. Cont.

Functional Platform	Target Compound Class	Typical Membrane and Electrode Materials	Operating Voltage and Current Density	Specific Energy Consumption (SEC) and Recovery	Operating pH Window and Feed Type	TRL	Rate-Limiting Thermodynamic and Engineering Constraints
Conductive and Reactive Membranes (Programmable Surface Gating)	Specialty biochemicals, complex isomeric mixtures, electroactive fermentation intermediates [124,125].	Membranes: Conductive polymer composites (PANI, PEDOT), CNT-doped matrices, or 2D lamellar MXenes/MOFs on PVDF scaffolds. Electrodes: Membrane acts directly as working electrode.	Voltage: Pulsed or variable (0.5–2.0 V). Current Density: <10 mA/cm² (low field required for gating).	SEC: 1.5–5.0 kWh/kg_{product} Recovery: 50–80% (high selectivity factor, moderate yield).	pH Window: 3.0–9.0 (dependent on polymer and nanomaterial stability). Feed Type: Highly pre-treated, low-fouling biorefinery streams.	2–3	Scalability and Mechanical Fatigue: Translating 2D interfacial materials from centimeter-scale coupons to square-meter industrial modules often results in defect propagation and loss of electrical uniformity under continuous stress. Mitigation: Requires hierarchical 3D cross-linking and roll-to-roll (R2R) casting methodologies.
		Membranes: Robust CEMs or gas-permeable hydrophobic membranes. Electrodes: Carbon brush/felt bio-anodes; stainless steel or Ni-alloy cathodes.	Voltage: Self-generated (0.3–0.6 V) or externally supplemented (<1.0 V). Current Density: 1–5 A/m²	SEC: 2.1–3.6 kWh/kg N (in balanced feeds); spikes above 100 kWh/kg in dilute matrices. Recovery: 70–95% (for NH₄⁺).	pH Window: 6.5–8.0 (strictly constrained by live microbial physiology). Feed Type: Raw, high-COD complex organics (slaughterhouse waste, manure, sewage).	3–4	Current Density Limitation: Biologically catalyzed electron flux generates low current densities (<5 A/m²). Driving industrial-scale transmembrane flux requires external voltage supplementation, which can erode net-positive energy balances. Mitigation: Requires high-surface-area 3D bio-anodes and strict C:N stoichiometric balancing.

Notes: **Note on Technology Readiness Levels (TRL):** The TRL assignments reflect the developmental maturity of each platform specifically for the recovery of biochemicals from real biological matrices, rather than idealized synthetic solutions. Assessments are scaled as follows: **TRL 1–3** (Fundamental research and lab-scale proof-of-concept, often constrained by material fabrication limits); **TRL 4–5** (Bench-to-pilot scale validation in relevant operational environments, addressing early-stage fouling and competitive ion transport); and **TRL 6–9** (Pre-commercial demonstration to full industrial integration, characterized by continuous operation, optimized specific energy consumption, and module-level hydrodynamic stability). A platform's TRL for bioseparation is frequently lower than its equivalent TRL for bulk desalination due to the compounded complexities of biofouling, dynamic speciation, and anodic oxidation.

4. Membrane Material Design and Interfacial Selectivity Engineering

The rapid evolution of electro-driven bioseparations has fundamentally shifted the focus of membrane material design from maximizing bulk ionic conductivity toward engineering programmable interfacial selectivity. Conventional ion-exchange membranes (IEMs) were conceptualized for desalination; their design prioritizes high fixed-charge density, minimal electrical resistance, and long-term stability in simple saline environments [126]. However, extracting bio-based chemicals from complex fermentation broths demands a fundamentally different material capability. Membranes must simultaneously discriminate among structurally identical organic analogues, dynamically adapt to fluctuating pKa and pH environments, and actively resist catastrophic fouling by proteins and extracellular polymeric substances (EPS).

This transition represents a broader paradigm shift in membrane physics. Traditional polymeric membranes function as passive, heterogeneous free-volume barriers where transport is dictated by static size exclusion or fixed Donnan potentials. In contrast, emerging electro-driven materials operate as *active electrochemical interfaces*. As conceptually illustrated in Figure 4, next-generation membranes synthesize sub-nanometer confinement, redox-active functionalities, and stimuli-responsive surface gating. Selectivity is no longer an intrinsic bulk property; it is an actively engineered phenomenon arising from the continuous interaction among the applied electric field, the membrane's nano-architecture, and the dynamic speciation of the target molecule.

To systematically evaluate these emerging architectures, it is necessary to clearly distinguish among the functional components of an electro-driven membrane system (EDMS): (1) the *polymer matrix*, which provides mechanical integrity and defines bulk ion-exchange capacity; (2) *conductive additives*, which establish internal electron transport pathways; (3) *interlayers and surface coatings*, which govern nanoscopic sieving and anti-fouling hydration kinetics; and (4) *electrode materials*, which drive the primary electrochemical gradients. Each component serves a distinct thermodynamic function and exhibits unique mechanical and chemical failure modes when exposed to complex biorefinery streams.

4.1. Nanoengineered and Two-Dimensional Confinement Interfaces

The integration of two-dimensional (2D) nanomaterials has revolutionized the ability to orchestrate molecular transport at the angstrom scale. Unlike traditional polymeric membranes, which rely on the tortuous and highly irregular free-volume pathways of cross-linked networks, 2D laminates (e.g., graphene oxide, MXenes) create highly deterministic, ordered lamellar galleries [127–129]. Within these sub-nanometer channels, the physics of bulk diffusion collapses. Transport is instead rigidly governed by localized electrostatic interactions, the stripping of molecular hydration shells, and intense interfacial polarization.

Graphene oxide (GO) established the foundation of this field, utilizing its tunable interlayer spacing and oxygen-rich functional groups to manipulate transport. By precisely modulating the electronegativity of the GO lamellae and restricting the interlayer distance to match the hydrated radii of target ions, researchers have engineered extreme steric-electrostatic sieving, achieving discrimination factors exceeding 90-fold between structurally similar competing anions [130].

However, the frontier of 2D electrified interfaces is currently dominated by transition metal carbides and nitrides (MXenes), specifically $\text{Ti}_3\text{C}_2\text{T}_x$. Unlike highly insulating GO, MXenes possess metallic-level electronic conductivity, enabling the membrane itself to function as a polarized electrode. This allows for electric field-assisted nanofiltration, where the membrane dynamically alters its sieving parameters based on the applied voltage. Applying a modest negative potential (e.g., -2.0 V) to an ultra-thin (~ 47 nm) MXene separation layer actively polarizes the interface, transforming it into an electrostatic

gate. This phenomenon can instantly amplify the rejection of target organic molecules (e.g., cationic dyes or charged metabolites) from a passive baseline of 26% to an active rejection of 98%, while allowing background inorganic salts to permeate freely [131,132].

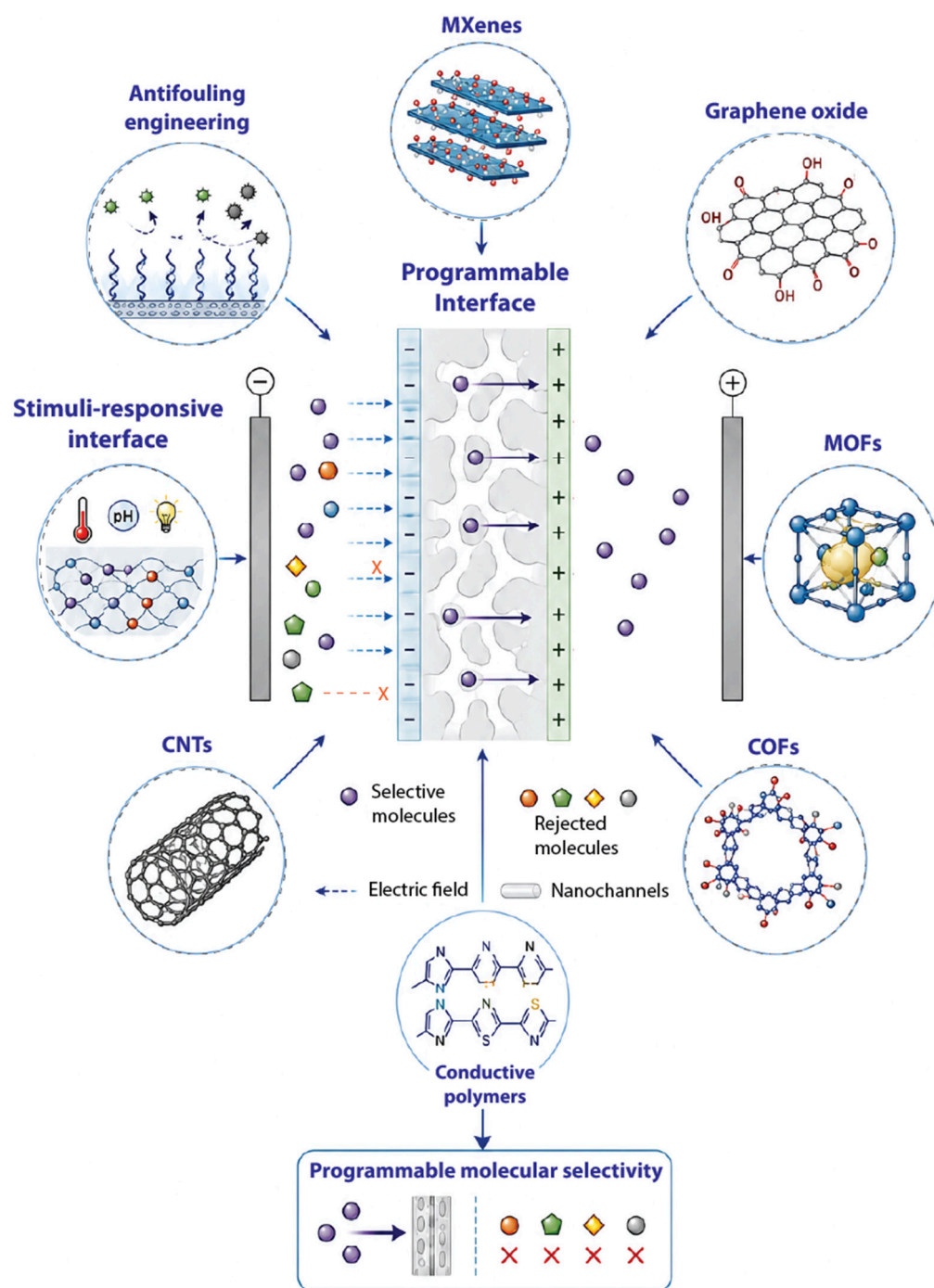


Figure 4. The architectural synthesis of active, programmable electrochemical interfaces. By integrating sub-nanometer spatial confinement (MXenes, graphene oxide, MOFs, COFs), highly conductive networks (CNTs, conductive polymers), and dynamic thermodynamic defenses (stimuli-responsive and anti-fouling engineering), next-generation membranes transcend passive size-exclusion to achieve precise, electrically programmable molecular discrimination.

Beyond simple separation, MXene interfaces represent the convergence of molecular sieving and electro-catalysis. Because these membranes possess excellent electron-donating capabilities, they can simultaneously drive highly selective faradaic reactions within the

confined nanopores. For example, by utilizing $\text{Ti}_3\text{C}_2\text{T}_x$ membranes as flow-through gas-diffusion cathodes, the localized Oxygen Reduction Reaction (ORR) forcibly shifts the boundary-layer pH to 8.0–10.0. This engineered pH microenvironment drives the speciation of aqueous ammonium (NH_4^+) directly into volatile ammonia (NH_3) as it passes through the lamellae, yielding exceptional extraction capacities ($>270 \text{ mgN/g}$) at specific energy consumptions as low as 0.73 kWh/kg N [133,134].

Flow-through confinement fundamentally circumvents the mass-transfer limitations of batch reactors, accelerating catalytic conversion kinetics by nearly 5-fold [135]. This electro-catalytic confinement has profound implications for process intensification. Highly functionalized MXenes are now being deployed as reactive interfaces to perform continuous in situ electrocatalytic hydrogenation (ECH) of biomass (e.g., converting furfural to furfuryl alcohol with $>96\%$ conversion and $>92\%$ selectivity) [136], and heavily doping them into bipolar membranes has been shown to amplify water-dissociation kinetics and proton recovery by 4.5-fold [137].

Complementing 2D laminates, highly crystalline networks such as Metal–Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs) provide rigid, mathematically defined pore geometries. While 2D materials rely on interlayer stacking, MOFs and COFs can be synthesized with tailored ligand-metal coordination to discriminate between nearly identical species. For example, embedding specific MOF architectures (e.g., SrCu_6Ser) within mixed-matrix membranes enables the precise separation of transition metals (e.g., isolating Cobalt over Nickel) based entirely on subtle differences in coordination chemistry rather than crude atomic size [124].

Engineering Trade-offs and Operational Constraints: Current literature frequently emphasizes the extreme selectivity of pristine 2D lamellar membranes and highly ordered MOFs under idealized laboratory conditions using low-salinity synthetic solutions [138–140]. However, translating these nanoconfined structures to real biorefinery broths exposes significant material vulnerabilities. In complex, unrefined fermentation media, 2D laminates are susceptible to interlayer swelling, osmotic delamination, humic acid intercalation, and pore blinding by amphiphilic proteins. Furthermore, under continuous voltage cycling, transition metal carbides ($\text{Ti}_3\text{C}_2\text{T}_x$) can undergo anodic oxidation, leading to structural degradation and loss of electronic conductivity. Advancing these materials toward industrial deployment requires moving beyond ultra-thin free-standing films. Research must prioritize hierarchical resilience—chemically cross-linking or covalently tethering 2D lamellae and MOF particles to porous, chemically resistant 3D polymeric scaffolds (e.g., PVDF, PTFE) to ensure module-scale reproducibility and mechanical stability against industrial shear stress and salinity.

4.2. Electrically Conductive Matrices

The incorporation of electrically conductive materials into membrane architectures represents one of the most profound departures from conventional separation engineering. Traditional polymeric membranes are electrically insulating, serving merely as passive barriers through which ionic current is carried exclusively by mobile permeants. In contrast, integrating conductive matrices (e.g., carbon nanotubes, 3D carbon frameworks, and inherently conductive polymers) transforms the membrane into an electronically active participant in the separation process [69,141]. These architectures actively dictate interfacial charge distribution, orchestrate localized electron transfer, and enable reactive separation mechanisms that seamlessly couple molecular migration with electrochemical transformation.

Carbon nanotubes (CNTs) and continuous 3D carbon frameworks (e.g., carbon aerogels, graphene foams) exemplify this paradigm. Their high aspect ratios facilitate the formation of percolated conductive networks within the polymer matrix, dramatically lowering

electrical resistance while providing atomically smooth internal channels that minimize frictional mass-transfer resistance [142–145]. Crucially, the high electronic conductivity of these matrices enables electro-thermal speciation control via localized Joule heating.

Rather than expending massive thermal energy to heat the entire bulk fluid, applying a moderate voltage (e.g., 15 V) across a highly conductive (e.g., >60 S/m) CNT-composite membrane generates intensely localized heating directly at the liquid–vapor interface. This precise thermal gradient actively forces the thermodynamic equilibrium of target species (such as shifting dissolved NH_4^+ to volatile NH_3) instantly at the boundary layer. By combining this electro-thermal speciation with extreme surface hydrophobicity, such systems achieve a nearly 5-fold amplification in mass transfer coefficients without the severe specific energy consumption associated with bulk distillation [146].

Beyond electro-thermal effects, conductive matrices serve as critical electron-transfer scaffolds for redox-coupled affinity separations. Conductive polymers such as polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) exhibit reversible redox states that dynamically alter their surface charge and molecular binding energies under an applied potential [147–150]. When hybridized with carbon nanostructures, these systems achieve extraordinary molecular discrimination.

For example, functionalizing CNTs with ferrocene-doped polyaniline (Fc-PANI) shifts the separation mechanism from simple capacitive deionization to targeted inner-sphere coordination. In its electrochemically oxidized state, the Fc-PANI matrix establishes intense, highly selective hydrogen bonding specifically with phosphate anions (HPO_4^{2-} , H_2PO_4^-). This faradaic synergy effortlessly overcomes the severe ionic competition of multi-component wastewaters, achieving extraction capacities of 35 mg/g at 1.2 V with near-100% molecular selectivity [151].

Even within hybrid or pressure-driven electro-filtration paradigms, the integration of conductive matrices fundamentally alters interfacial thermodynamics. Doping conventional matrices (e.g., polyethersulfone) with multi-walled carbon nanotubes and conductive silver nanoparticles radically amplifies the localized negative charge density of the membrane surface. This synthesized electronegativity, coupled with tunable sub-nanometer porosity, establishes a dual steric-electrostatic barrier capable of fractionating volatile fatty acids (VFAs) with rejection rates approaching 87% for mixed VFA streams while sustaining high solvent permeability (>60 LMH/bar) [152].

Engineering Trade-offs and Operational Constraints: While integrating electronic conductivity into membrane matrices offers distinct selectivity advantages [66,153,154], it introduces specific electrochemical limitations. As the electronic conductivity of a membrane approaches that of the surrounding electrolyte, the system becomes increasingly susceptible to parasitic Faradaic reactions. Instead of driving the selective electromigration of the target biochemical, applied electrical energy can be consumed by localized water splitting, radical generation, and the irreversible electro-oxidation of target organic molecules. Furthermore, cyclic redox-swelling of inherently conductive polymers (such as PANI and PPy) induces mechanical stress, which can lead to binder dissolution, polymer delamination, and progressive decay of ion-exchange capacity over extended operation (>500 h). To mitigate these limitations, future designs should focus on anisotropic conductive architectures—membranes engineered with high conductivity along specific trans-membrane transport vectors, but electronically insulated against bulk parasitic electron transfer to the surrounding fluid.

4.3. Stimuli-Responsive Architectures

Perhaps the most sophisticated frontier in electrified membrane science is the synthesis of architectures capable of dynamically adapting their transport thermodynamics in

real time. Conventional membranes are structurally rigid; their pore sizes, bulk charge densities, and dielectric constants are permanently fixed during casting. This static nature is fundamentally incompatible with live biological systems, where the rheology, salinity, and molecular speciation of the feed fluctuate continuously. Stimuli-responsive systems fundamentally disrupt this limitation by functioning as dynamic electrochemical interfaces capable of actively modifying pore accessibility, surface polarity, or binding affinities in response to external environmental triggers [155–158].

pH-responsive architectures are the most mature iteration of this concept. By integrating functional groups with precise acid dissociation constants (e.g., carboxylates, amines) into the polymer matrix, the membrane can reversibly protonate or deprotonate in response to localized pH gradients. For complex bioseparations, this creates a profound, auto-catalytic feedback loop. Because the target bio-molecules (e.g., volatile fatty acids, zwitterionic amino acids) also undergo speciation shifts, a pH-responsive membrane actively evolves its Donnan potential synchronously with the target molecule's charge state.

Recent advances have successfully coupled pH-responsiveness with phase-transition phenomena. For instance, modifying magnetic graphene oxide with pH-responsive zwitterionic copolymers (e.g., poly(AA-b-SBMA)) creates ultrafiltration interfaces that actively expand or collapse their hydration spheres based on the feed pH. Modulating the pH across the critical transition point (e.g., shifting from pH 3 to 8) induces a physical swelling of the zwitterionic brushes. This conformational shift literally physically ejects adsorbed bio-macromolecules (e.g., bovine serum albumin) from the surface, achieving flux recovery values exceeding 70% without the use of harsh, energy-intensive chemical clean-in-place (CIP) protocols [159].

Similar phase-responsive mechanisms are now being engineered into lignin-grafted amphoteric surfactants, which exploit combined pH and Upper Critical Solution Temperature (UCST) transitions to simultaneously drive the separation and rapid low-temperature co-precipitation of costly cellulase enzymes, dramatically reducing the downstream economic penalty of lignocellulosic hydrolysis [160].

Moving beyond pH, redox-switchable and electro-responsive gating architectures provide an unprecedented level of external, programmatic control. Rather than relying on the passive chemical environment of the feed, these membranes utilize electroactive functional groups or highly polarizable nanostructures that physically alter their electronic structures under an externally applied voltage [161,162]. Adjusting the applied potential dynamically alters the thickness of the interfacial electric double layer, effectively opening or collapsing sub-nanometer pathways. This converts the membrane from a static barrier into an electronically controlled molecular valve, enabling real-time, adaptive correction of selectivity during prolonged fermentation runs.

Engineering Trade-offs and Operational Constraints: While proof-of-concept “smart” membranes responding to external stimuli (such as light, magnetic fields, or thermal shifts) demonstrate innovative gating mechanisms [34,66,155,159], their industrial translation is frequently limited by response kinetics and mechanical durability. The timescale required for polymer brushes or hydrogel matrices to structurally swell, collapse, or alter charge density is often orders of magnitude slower than the fluid residence time in high-throughput industrial modules. Furthermore, repeated structural expansion and contraction generate internal mechanical shear, which can lead to micro-cracking and loss of permselectivity over extended cyclic operation. For scalable bioseparations, research must transition from slow physical polymer swelling toward instantaneous electronic surface gating, where selectivity is governed by rapid polarization of the electrical double layer without requiring physical deformation of the polymer matrix.

4.4. Built-In Anti-Fouling Through Interfacial Engineering

Biofouling represents a primary operational bottleneck governing the industrial implementation of electro-driven bioseparations. The fouling paradigm in biorefining differs fundamentally from the inorganic scaling (e.g., CaCO_3 , CaSO_4) typically encountered in seawater desalination. Fermentation broths are dense suspensions of highly cohesive, amphiphilic biological foulants—extracellular polymeric substances (EPS), denatured proteins, lipid bilayers, and cellular debris [163,164]. Under the driving force of an applied electric field, these bio-macromolecules are electro-migrated and deposited onto the membrane surface, increasing electrical resistance and impairing interfacial selectivity. Consequently, anti-fouling must be engineered as an intrinsic thermodynamic property of the electrified interface rather than relying solely on post-operational chemical cleaning.

Thermodynamic defense against biofouling relies primarily on engineering interfacial hydrophilicity to manipulate boundary-layer hydration energy. The objective is to establish an energetically unfavorable barrier against the adsorption of hydrophobic protein domains. By integrating hydrophilic nanomaterials or grafting zwitterionic polymer brushes onto the membrane surface, the interface binds water molecules with high affinity, forming a structured hydration layer. For a protein to adhere to the membrane, it must thermodynamically displace this hydration layer. If the free energy required to strip the water layer exceeds the adsorption energy of the protein, non-specific binding is suppressed.

Complementing hydration thermodynamics, surface charge density and topographical engineering provide essential mechanical defenses. While optimizing Donnan exclusion requires high fixed-charge density, excessive surface charge can accelerate the electrostatic accumulation of oppositely charged bio-macromolecules. Therefore, surface charge density must be balanced to maintain target ion flux while minimizing electrostatic foulant tethering. Morphologically, hierarchical nanoscale roughness must be optimized to disrupt local hydrodynamic boundary layers, preventing the formation of stagnant zones where EPS typically nucleates.

The engineering frontier merges these physical modifications with the electrical capabilities of the system. Advanced architectures are engineered for active self-cleaning through electro-responsive mechanisms—utilizing pulsed reversed polarity, localized Faradaic micro-bubble generation (H_2 or O_2 evolution), or induced isoelectric point shifting to disrupt and detach accumulated biofilms before consolidation occurs.

Engineering Trade-offs and Operational Constraints: The membrane literature predominantly evaluates anti-fouling efficacy by measuring hydraulic flux preservation or visual reductions in surface deposition [163,165,166]. In electro-driven membrane systems, however, hydraulic permeability alone is an incomplete indicator of performance. A membrane may maintain constant fluid permeability while accumulating a microscopically thin, electrochemically insulating monolayer of denatured protein or EPS. This organic boundary layer can mask fixed surface charges, alter local dielectric constants, and increase trans-membrane Ohmic resistance, leading to a collapse in permselectivity and an exponential increase in specific energy consumption (kWh/kg). Consequently, industrial benchmarking of anti-fouling architectures must move beyond simple flux-decline metrics and evaluate performance strictly through the long-term preservation of molecular selectivity, current efficiency, and SEC stability during extended operation in authentic biological broths.

5. Recovery Pathways for Bio-Based Chemicals from Complex Aqueous Systems

The ultimate validation of electro-driven membrane technologies lies not in their theoretical permselectivity within pristine, synthetic solutions, but in their techno-economic viability when deployed in chemically hostile, multi-component biological matrices. Un-

like conventional electro-separations optimized for bulk water desalination, bio-based separations are governed by the mandate of molecular resource recovery. The objective is to selectively extract highly dilute, high-value biochemicals from dense heterogeneous broths while simultaneously preserving the rheological and biological integrity of the feed [73,167].

The thermodynamic complexity of this task cannot be overstated. Industrial fermentation broths and anaerobic digestates are chaotic environments containing mixtures of weak organic acids, zwitterionic peptides, uncharged sugars, volatile alcohols, competing inorganic salts, extracellular polymeric substances (EPS), and suspended cellular debris. Consequently, separation performance is not merely a function of applied voltage or bulk membrane morphology; it is dictated by the dynamic, highly competitive physicochemical interactions occurring within the interfacial boundary layer.

The recovery pathway must therefore be engineered around the fluctuating thermodynamic identity of the target molecule rather than the mechanical configuration of the hardware. Weak aliphatic acids demand highly precise localized pH manipulation to control their dissociation states; amino acids require isoelectric point (pI) trapping; and neutral fermentation solvents benefit indirectly from the electro-driven extraction of inhibitory ionic co-metabolites. The integration of these targeted recovery pathways within continuous biorefining loops and the definitive benchmarking of their performance metrics and Technology Readiness Levels (TRL) is synthesized in Table 4.

Engineering Trade-offs and Operational Constraints: The bioseparation literature frequently reports high extraction efficiencies derived from idealized, binary synthetic solutions. However, demonstrating a >90% recovery rate for a target biochemical in pure water provides limited predictive value for industrial scale-up. In authentic industrial broths, competitive electromigration by highly mobile background salts (K^+ , Cl^- , PO_4^{3-}) significantly alters transmembrane current distribution, while EPS and dissolved organic matter instantly modify the membrane's interfacial dielectric constant and electrical resistance. Furthermore, a recovered stream is not industrially viable unless it meets strict downstream requirements for concentration factor, product purity, and chemical stability. To establish benchmark reliability, future research must evaluate EDMS using raw or pre-treated industrial fermentates, standardizing reporting metrics across compound classes to include specific energy consumption ($kWh/kg_{product}$), current efficiency (η), concentration factor, and long-term permselectivity decay under realistic competitive conditions.

5.1. Recovery of Aliphatic Organic Acids

Aliphatic organic acids—including lactic, succinic, acetic, and mixed volatile fatty acids (VFAs)—constitute the foundation of the bio-based chemical industry, serving as vital platform precursors for biodegradable polymers and specialty solvents [1,23,24,26,59]. While microbial synthesis of these compounds has reached high metabolic efficiencies, their downstream recovery remains the dominant techno-economic bottleneck. Conventional downstream processing relies heavily on calcium-induced precipitation (which generates massive volumes of stoichiometric gypsum waste) or highly energy-intensive reactive distillation.

Electro-driven extraction fundamentally bypasses these thermodynamic and environmental penalties by exploiting the weak-acid chemistry of these molecules. Because aliphatic acids continuously transition between neutral, protonated forms ($R-COOH$) and dissociated, anionic forms ($R-COO^-$), their electrophoretic mobility is not static; it is rigorously dictated by the relationship between the localized pH and the molecule's acid dissociation constant (pK_a). Electromigration strictly acts upon the ionized fraction (α). Consequently, successful extraction requires the simultaneous, active management of trans-

membrane proton flux and localized acid-base equilibria to continuously pull the target molecule into its highly mobile anionic state.

For bulk platform chemicals like lactic and succinic acid, electrodialysis and bipolar membrane systems have achieved immense process intensification through in situ product recovery (ISPR). Lactic and succinic acid fermentations are notoriously susceptible to severe product inhibition [28,54,78,82,85]; as the acid accumulates, the reactor pH crashes, suppressing microbial metabolism. By directly coupling the fermenter to an electro-driven membrane loop, the dissociated acid species are continuously electro-migrated out of the broth. This dynamically stabilizes the bioreactor pH without the need for constant, massive volumetric additions of alkaline buffers, boosting total volumetric productivity and yielding target acids at specific energy consumptions frequently competitive with or superior to thermal evaporation (e.g., 0.5–2.0 kWh/kg).

The engineering challenge increases significantly when transitioning from bulk extraction to the precise fractionation of complex VFA streams [24,25,57]. Anaerobic digestion and mixed-culture fermentations yield crude mixtures of acetate, propionate, butyrate, and valerate. Isolating these structural analogues into discrete, chemical-grade fractions represents a massive opportunity for circular waste valorization. However, differentiating between these homologues using standard electro-driven matrices is exceptionally difficult due to their nearly identical charge-to-mass ratios and overlapping pKa values.

A common limitation in current VFA recovery research is the assumption that structural analogues (e.g., acetate vs. propionate) can be efficiently fractionated using standard ion-exchange membranes simply by tuning bulk current density. Because their pKa values are nearly indistinguishable (~4.76 vs. ~4.87), standard electrostatic driving forces cannot differentiate between them thermodynamically; they co-migrate almost identically [58,168,169]. To achieve chemical-grade fractionation of homologous aliphatic acids, membrane engineering must move beyond purely charge-based exclusion. Architectures must integrate sub-nanometer steric confinement or specific lipophilic affinity ligands capable of discriminating based strictly on aliphatic chain length and hydrophobic interactions.

5.2. Recovery of Nitrogenous Biochemicals

Nitrogen-containing biomolecules introduce a formidable layer of thermodynamic complexity to electro-driven separations [59,116,133]. Unlike aliphatic organic acids that simply shift between neutral and anionic forms, amino acids, peptides, and complex nitrogenous metabolites are amphoteric. They possess both acidic and basic functional groups, allowing them to exist as cationic, anionic, or zwitterionic species depending on the surrounding pH. Their effective electrophoretic mobility is therefore not a static physical property; it is an active variable strictly governed by the relationship between the localized boundary-layer pH and the molecule's isoelectric point.

Because net molecular charge approaches zero at the isoelectric point, molecules become functionally immune to electromigration despite the presence of an applied electric field. Consequently, successful separation requires high-precision manipulation of the pH gradients directly at the membrane interface. Bipolar membrane electrodialysis (BMED) has emerged as an exceptionally potent platform for this task, as the continuous electrochemical generation of protons and hydroxide ions allows for the in situ modulation of amino acid speciation without the addition of exogenous salts. Recent state-of-the-art applications demonstrate that BMED can directly convert amino acid hydrochlorides (e.g., L-ornithine monohydrochloride) to their pure, zwitterionic free-base forms, achieving conversion ratios exceeding 96% with remarkably low specific energy consumptions of 0.31 kWh/kg [170].

This strategy is particularly powerful for fractionating complex, homologous mixtures. By stabilizing the feed pH precisely between the isoelectric points of two competing

molecules, one species can be driven into a highly mobile cationic state while the other is electrostatically trapped. For example, by fixing the operational pH at 10.0, electrodialytic systems have successfully fractionated 1,5-pentanediamine (PDA, average net charge +1.5) from L-arginine (net charge zero), achieving >60% selective recovery with a minimal energetic footprint of ~3.0 kWh/kg [171].

Engineering Trade-offs and Operational Constraints: While isoelectric focusing and precise pH-trapping provide high theoretical selectivity for nitrogenous biochemicals, their industrial application encounters a specific physical limitation: isoelectric precipitation. When target proteins or amino acids are forced into their isoelectric state at the membrane interface to prevent cross-migration, their aqueous solubility drops to its thermodynamic minimum. In concentrated industrial broths, this can induce localized crystallization and surface scaling directly on the ion-exchange membrane, leading to severe flux decline and an increase in electrical resistance. To prevent interfacial precipitation, system design must integrate sub-nanometer steric or affinity exclusion mechanisms, allowing amino acids to be fractionated while remaining in charged, highly soluble states away from their isoelectric thresholds.

5.3. Process Intensification Through Selective Inhibitor Removal

Perhaps the most transformative industrial application of electro-driven membrane technology lies not in the direct downstream extraction of the final product, but in upstream process intensification. Traditional downstream processing architecture treats fermentation and product recovery as rigidly sequential unit operations, allowing toxic, inhibitory metabolites to accumulate in the bioreactor until the microbial metabolism is completely suppressed. In modern biorefineries producing neutral solvents—such as the Acetone–Butanol–Ethanol (ABE) fermentation process—this accumulation is the primary bottleneck dictating economic viability.

During ABE fermentation, solventogenic clostridia generate massive quantities of intermediate organic acids (acetic acid, butyric acid) during the primary acidogenic phase [172,173]. As these dissociated acids accumulate, they adhere to cell membranes and catastrophically collapse the intracellular pH gradients required for ATP synthesis, permanently capping the maximum achievable solvent titer at a mere ~2% [174,175].

Electro-driven separations fundamentally resolve this biological limitation by serving as an active in situ process regulator rather than a terminal purification step. By integrating an extractive electrodialysis loop directly into the fermentation circuit, dissociated acetate and butyrate are continuously electro-migrated out of the broth as rapidly as they are synthesized [12,51]. This targeted extraction buffers the bioreactor pH without the addition of massive volumes of caustic chemicals, alleviating end-product toxicity in real time. By preventing the acid-crash, the productive operating window of the fermentation is drastically extended, allowing continuous, high-cell-density bioreactors to achieve volumetric productivities (g/L/h) that eclipse the limitations of conventional batch operations.

The thermodynamic elegance of this strategy is that removing relatively small quantities of ionic inhibitory precursors requires a fraction of the specific energy (kWh/kg) needed to recover the final, uncharged solvent via thermal distillation. Consequently, the selective electro-removal of toxic metabolites indirectly amplifies the yield of electrically neutral target molecules, slashing the overall process energy intensity.

Engineering Trade-offs and Operational Constraints: While in situ extractive electrodialysis for inhibitor removal is theoretically robust, its execution in live fermentation systems must account for competitive ion transport. Standard anion exchange membranes cannot thermodynamically distinguish between a monovalent inhibitory organic acid (e.g., acetate) and vital multivalent microbial nutrients (e.g., phosphate, sulfate) [176,177].

Continuous electrodialytic extraction can therefore indiscriminately strip the bioreactor of essential trace minerals and anions, eventually leading to nutrient depletion and stalling microbial growth despite the successful removal of toxins. To maintain fermentation stability, in situ extraction loops must incorporate monovalent-selective anion exchange membranes or charge-mosaic interfaces, ensuring that inhibitory monovalent carboxylates are removed while multivalent nutritional components remain retained within the active broth.

5.4. Nutrient and Carbon Recovery: Closing the Biorefinery Loop

Beyond the extraction of high-value platform chemicals, the ultimate sustainability of the biorefinery hinges on the circular management of its residual effluents. Conventional wastewater treatment facilities approach fermentation effluents—which are dense in nitrogen, phosphorus, and residual dissolved organic carbon—as environmental liabilities. They expend massive thermal and electrical energy (typically 1.0–2.0 kWh/m³ for aeration alone) to destructively oxidize organics and convert reactive nitrogen back into inert N₂ gas via nitrification-denitrification [178,179].

Electro-driven membrane technologies fundamentally invert this paradigm, treating residual effluents not as waste, but as highly concentrated mineral and carbon reservoirs ripe for molecular valorization. Nutrient recovery via electro-separation is governed by the selective electromigration of specific ionic states [180]. For nitrogen, ammonium (NH₄⁺) is effectively extracted using cation exchange membranes or membrane capacitive deionization (MCDI), frequently achieving concentration factors exceeding 10-fold at highly competitive energy expenditures of 1.0 to 4.0 kWh/kg N [107,110,115,125].

For phosphorus, extraction relies on manipulating the pK_a boundaries of orthophosphate. Because phosphate transitions from monovalent (H₂PO₄[−]) to divalent (HPO₄^{2−}) and trivalent (PO₄^{3−}) states as pH increases, localized pH control within the membrane boundary layer allows operators to selectively dictate its transmembrane mobility and subsequent precipitation kinetics. When coupled with sacrificial metallic electrodes (e.g., magnesium or iron), these systems effortlessly integrate electro-concentration with in situ crystallization, yielding high-purity, solid-state vivianite or struvite fertilizers directly from the effluent [104,176,181].

Concurrently, residual carbon recovery targets the dilute, mixed volatile fatty acids (VFAs) and unfermented organic anions remaining after primary product extraction. While purifying these highly dilute species individually is thermodynamically prohibitive via distillation, electrodialytic concentration pools them into a singular, energy-dense carbon concentrate. This upgraded carbon stream is seamlessly redirected upstream as a premium feedstock for secondary biological conversion (e.g., polyhydroxyalkanoate [PHA] synthesis or methanogenesis), effectively closing the biorefinery mass balance.

Engineering Trade-offs and Operational Constraints: A primary operational challenge governing electro-driven nutrient recovery from raw digestates is inorganic mineral scaling [182,183]. Fermentation effluents are frequently saturated with divalent cations, particularly Ca²⁺ and Mg²⁺. When electrodialytic systems induce localized alkaline boundary layers to drive phosphate recovery or deprotonate organic acids, they can trigger the crystallization of calcium carbonates and magnesium phosphates directly upon the ion-exchange membrane surface. This internal scaling blocks ion-exchange sites, increases Ohmic resistance, and accelerates membrane degradation. To maintain continuous operation in unrefined effluents, system design must incorporate scaling-resilient strategies—such as asymmetric pulsed-reversed polarity, monovalent-selective permselective coatings, and sub-isoelectric boundary-layer buffering to repel divalent scaling precursors.

5.5. Continuous Fermentation-Coupled Systems: The Fully Integrated Electro-Biorefinery

The integration of electro-driven membrane systems directly with operating bioreactors represents the definitive leap toward continuous, next-generation biomanufacturing. Historically, industrial biotechnology has been crippled by the batch-processing paradigm, which rigidly segregates biological synthesis from physicochemical purification [184,185]. This architecture is inherently self-limiting: as target metabolites accumulate in the bioreactor, they inevitably induce severe osmotic stress, disrupt intracellular pH, and permanently crash the microbial metabolism, capping volumetric productivity.

Continuous in situ product recovery (ISPR) completely dismantles this biological ceiling. By physically coupling an electrodialytic or bioelectrochemical membrane loop to the live fermenter, the target molecules—such as lactic or succinic acid—are continuously extracted from the broth at the exact rate of their microbial biosynthesis. This establishes a perfect thermodynamic equilibrium within the reactor. Because the inhibitory product is never allowed to accumulate, the exponential growth and production phases of the microbes can be sustained indefinitely.

Consequently, fermentation-coupled systems have demonstrated the ability to increase volumetric productivities (g/L/h) by over 300% compared to equivalent batch processes, while entirely eliminating the massive CapEx associated with intermediate storage tanks and the OpEx of external alkaline buffer dosing. Electro-driven membranes are uniquely suited for ISPR because they offer unprecedented digital control [12,24,34,186]. Unlike purely pressure-driven separations (which suffer from rigid, irreversible fouling) or thermal separations (which are biologically lethal), the transport driving force in an electrified membrane can be adjusted instantaneously.

As the microbial growth curve transitions, the applied voltage or current density can be adaptively modulated in real time to match fluctuating product titers, ensuring that the extraction rate perfectly mirrors the biological synthesis rate. The culmination of this approach is the fully integrated electro-biorefinery [186]. In this conceptual framework, the membrane ceases to be a mere separation barrier and becomes the central cyber-physical interface of the plant—simultaneously extracting products, recycling essential nutrients back to the biomass, regulating reactor pH via localized water dissociation, and continuously transmitting real-time electrochemical impedance data to AI-driven process control algorithms.

Engineering Trade-offs and Operational Constraints: Despite the theoretical advantages of continuous ISPR, directly routing live fermentation broth through the narrow spacer channels of an industrial electrodialysis stack introduces specific biophysical challenges. The hydrodynamic shear stress generated within conventional stacks can cause cellular damage or lysis, while intense localized electric fields at the membrane interface ($>10^4$ V/m) can induce cell electroporation and loss of viability. Furthermore, uncontrolled electromigration can deplete essential trace minerals (Co^{2+} , Fe^{2+}) required for enzymatic activity. To ensure long-term stability in fully integrated biorefineries, module architectures must physically decouple live biomass from the primary electric field—utilizing zero-shear microfiltration pre-stages or diffusion-limited conductive hydrogel interfaces that permit target metabolite extraction while preserving cellular viability and trace nutrient balances.

Table 4. Empirical Performance Metrics and Engineering Bottlenecks of Electrified Bioseparations.

Target Molecule	Feed Stream Complexity	Electro-Driven Process	Dominant Selectivity Mechanism	Typical Recovery (%)	Selectivity Factor	Specific Energy Consumption (kWh/kg)	TRL	Primary Technical Bottleneck	Refs.
Lactic Acid	High (Candy waste/acid whey)	NF-BMED hybrid systems	Speciation electromigration	46–70%	High (sugar exclusion)	0.8–1.2	6–7	Protein interface fouling	[53,82]
Succinic Acid	High (Fermentation broth)	Electrodeionization (EDI)	Dielectric-Donnan exclusion	94–96%	3.5 (vs. acetate)	1.5–2.5	5–6	Interfacial precipitation	[79,85]
Acetic Acid	Moderate (Gas fermenter)	BPMED/RO-ED hybrid	Proton-coupled transport	97–99%	High (vs. neutrals)	0.37–1.1	6–7	Intense proton back-leakage	[26,77]
Mixed VFAs	High (Anaerobic digestate)	ED–membrane contactor	Electromigration and stripping	55–65%	>5.0 (vs. nutrients)	0.40–0.97	5–6	Divalent mineral scaling	[80,84,86]
Propionic Acid	High (Mixed culture broth)	Electrodialysis (AEM)	Mobility electromigration	50–60%	1.5 (vs. acetate)	2.1–3.5	4–5	Overlapping pKa bounds	[23,75]
Butyric Acid	High (Anaerobic broth)	Capacitive Deionization	Reversible double-layer	70–80%	2.5 (vs. acetate)	1.2–1.8	4–5	Carbon electrode oxidation	[100]
Citric Acid	High (Aspergillus broth)	Electrodialysis stack	Multivalent Donnan effect	75–85%	2.7 (vs. monovalents)	4.5–5.1	5	Concentration polarization	[76]
Amino Acids	High (Protein hydrolysate)	BMED/pH-tuned ED	Amphoteric pI trapping	60–96%	>10 (pI-focused)	0.31–3.0	5–6	Interfacial crystallization	[171,187,188]
Peptides	Severe (Whey protein hydrolysate and human plasma)	ED–Ultrafiltration	Electrophoretic size gating	40–55%	3.0–5.0 (by charge)	3.5–6.0	4	Severe gel-layer fouling	[189,190]
Ammonium	Moderate (Wastewater)	Flow-Electrode CDI	Reversible EDL entrapment	60–95%	1.5–2.5 (vs. cations)	0.45–1.87	5	Low current density limits	[107,191,192]
Phosphate	High (Digestate permeate)	MCDI (Biochar/PANI)	Inner-sphere complexation	65–80%	>5.4 (vs. anions)	2.45–4.85	4–5	Co-ion scaling interference	[103,151,193]
Organic Carbon	High (Industrial waste)	Multi-stage BMED	Charge-regulated recovery	50–70%	Variable	1.0–2.5	4	Complex organic adsorption	[87,97]
Ethanol	High (Yeast fermentation)	Extractive ED loop	Selective salt/acid stripping	90–95% (Yield)	High (ion vs. neutral)	0.5–1.5 (Indirect)	5–6	Nutrient depletion starvation	[174,175]
Butanol	High (Clostridial broth)	Extractive ED/BMED	Volatile acid extraction	>300% (Prod.)	High (ion vs. neutral)	1.2–2.2 (Indirect)	5	Electroporation cell lysis	[174,175]
L-Malic Acid	High (Beverage industry wastewater; dark liquid with sugars, minerals, and organic salts)	Two-stage CED and BMED (BP/C)	Electromigration and water splitting	93–97%	Low (competes directly with other organic anions; requires final chromatography step)	1.15–1.91	4–5	Overconsumption of energy due to anionic impurities and lack of permselectivity	[194]

Table 4. Cont.

Target Molecule	Feed Stream Complexity	Electro-Driven Process	Dominant Selectivity Mechanism	Typical Recovery (%)	Selectivity Factor	Specific Energy Consumption (kWh/kg)	TRL	Primary Technical Bottleneck	Refs.
Fumaric Acid	High (Fermentation broth with glycerol, acetic acid, citric acid, mannitol)	Bipolar electrodialysis (EDBM)	Electromigration (size/charge dependent)	40–50% (broth)	Moderate (acetate and chloride compete; cordycepic acid leaks)	7.3	4	Cake-deposition fouling from solutes and co-transport of competitors	[195]
Methionine	High (Mother liquor from hydantoin pathway; sodium carbonate/NaOH)	Bipolar Membrane Electrodialysis (BMED)	pH-controlled speciation	91.8–97.1%	High (98.7–99.9% purity via precise pH control)	1.7–2.16	5–6	Amphoteric leakage due to protonation if pH drops below isoelectric point	[196]
Succinic Acid	High (Pre-treated fermentation broth with unreacted glycerol and lactose)	Large-scale Bipolar Membrane Electrodialysis (EDBM)	Electromigration and water splitting	~47% (actual broth)	Moderate (monocarboxylic acids compete)	1.5–4.88	5	Membrane fouling from biomass/salts causing sharp flux decline	[28]

Notes: **Abbreviations:** **AEM**, Anion Exchange Membrane; **BMED/BPMED/EDBM**, Bipolar Membrane Electrodialysis; **BP/C**, Bipolar/Cation Membrane Configuration; **CDI**, Capacitive Deionization; **CED**, Conventional Electrodialysis; **ED**, Electrodialysis; **EDI**, Electrodeionization; **EDL**, Electrical Double Layer; **MCDI**, Membrane Capacitive Deionization; **NF**, Nanofiltration; **PANI**, Polyaniline; **pI**, Isoelectric Point; **pKa**, Acid Dissociation Constant; **RO**, Reverse Osmosis; **SEC**, Specific Energy Consumption; **TRL**, Technology Readiness Level; **VFAs**, Volatile Fatty Acids.

6. System-Level Energetics, Sustainability, and Techno-Economic Performance

The scientific success of electro-driven membrane technologies is ultimately dictated by their macro-scale economic and environmental viability, rather than their isolated permselectivity in a laboratory beaker. While the preceding sections focused on the fundamental physics of interfacial selectivity, industrial implementation is governed by a ruthless, multi-dimensional optimization problem: balancing energy dissipation, volumetric productivity, product purity, capital expenditure (CapEx), and lifecycle carbon impact [11].

A nanocomposite membrane capable of achieving unprecedented discrimination between structural isomers remains industrially irrelevant if its electrical resistance inflates the specific energy consumption, or if its fragility necessitates frequent module replacement. Conversely, modest improvements in continuous, in situ molecular extraction can generate massive economic dividends if they eliminate the need for downstream thermal distillation or bypass the stoichiometric generation of solid chemical waste.

The defining thermodynamic advantage of electro-driven systems is their inherent coupling to electrical energy rather than latent heat. However, the simple act of electrification does not automatically guarantee sustainability. The true measure of process efficiency is how flawlessly electrical work is converted into the targeted electromigration of a biochemical, rather than being parasitically dissipated through bulk water dissociation, Ohmic heating (Joule losses), non-selective co-ion migration, or the overcoming of severe concentration polarization boundary layers [40,55,197,198].

Consequently, electro-driven bioseparations must be analyzed not as isolated unit operations, but as integrated cyber-physical components of the broader biorefinery flow-sheet. The techno-economic and thermodynamic characteristics comparing these electrified pathways to conventional thermal and chemical separations are benchmarked in Table 5.

6.1. The Macro-Scale Tradeoff: Energy, Purity, and Productivity

At the laboratory scale, performance is frequently reduced to isolated metrics: membrane flux, recovery percentage, or selectivity factor. These parameters are fundamentally flawed when extrapolated to industrial scale because they ignore the inescapable thermodynamic linkage between them [11]. Specific Energy Consumption (SEC)—expressed as kWh/kg_{product}—is the most critical system-level metric. However, SEC is meaningless in a vacuum. A system reporting an exceptionally low SEC (e.g., <0.5 kWh/kg) may only achieve this by operating at extremely low current densities, resulting in sluggish mass transfer that requires massive, economically unviable membrane surface areas (inflated CapEx) to meet industrial production targets.

Conversely, attempting to maximize volumetric productivity by aggressively ramping up the applied current density forces the system past its limiting current. This triggers severe concentration polarization, localized pH shifts at the membrane interface, and massive Ohmic resistance [199]. The electrical energy is no longer used to transport the target molecule; it is wasted on parasitic water splitting and heating the surrounding broth. Therefore, maximizing flux invariably destroys specific energy efficiency.

Product purity introduces the final constraint. Achieving chemical-grade purity from a complex broth typically requires multiple sequential electro-fractionation stages or driving the target molecule over intense electrostatic barriers. Both strategies exponentially inflate the system's energy requirements.

To overcome these competing constraints, future system-level engineering must transition from optimizing single variables toward machine-learning-guided Pareto front optimization [200]. Implementing robust Pareto optimization in real biorefinery loops requires standardizing three core parameter sets: (1) data inputs, including real-time feed viscosity,

ionic conductivity, background salt molarity, and target molecule pKa; (2) control variables, specifically applied voltage, current density, pulse-reversal frequency, and cross-flow velocity; and (3) validation datasets, which must track product purity, current efficiency (η), membrane ion-exchange capacity (IEC) decay, and total SEC over extended operational cycles (>1000 h). Identifying the exact operational threshold where CapEx (membrane area), OpEx (energy consumption), and downstream purity are balanced against the specific market value of the biochemical is essential for commercial viability.

6.2. Decarbonization Potential, Lifecycle Assessment, and UN SDG Alignment

The decarbonization potential of electro-driven bioseparations fundamentally relies on bypassing the latent heat of vaporization. Biorefinery streams are overwhelmingly dilute (>90% water). Conventional downstream processing—such as multi-effect evaporation and distillation—demands massive thermal energy input because the energy scales with the vast volume of bulk water, rather than the mass of the dilute target molecule [201,202]. Electro-driven systems perfectly invert this thermodynamic penalty: electrical work acts only upon the charged target molecule, leaving the bulk water phase essentially untouched. By transitioning from bulk phase change to targeted molecular migration, electro-separations can routinely reduce the energy footprint of recovery by 50–80% compared to thermal baselines.

Furthermore, electrification eliminates the Scope 1 emissions associated with on-site fossil-fueled boilers. However, electrification is not inherently carbon-neutral. To accurately evaluate environmental sustainability, the total carbon footprint (CF_{total} , expressed as $\text{kg}_{\text{CO}_2}/\text{kg}_{\text{product}}$) must be modeled as a function of specific energy consumption and regional grid carbon intensity (EF_{grid} , $\text{kg CO}_2 \text{ eq/kWh}$), combined with the embodied emissions of membrane manufacturing and module disposal ($CF_{embodied}$):

$$CF_{total} = (SEC \times EF_{grid}) \times CF_{embodied}$$

Replacing a natural-gas evaporator with an electrodialysis stack powered by a fossil-heavy electrical grid ($EF_{grid} > 0.7 \text{ kg CO}_2 \text{ eq/kWh}$) simply shifts emissions upstream, offering minimal climate benefit. Rigorous, cradle-to-grave Life Cycle Assessment (LCA) is therefore mandatory to validate true decarbonization potential.

When powered by low-carbon or renewable electricity, EDMs directly advance the objectives of the 2023 United Nations Sustainable Development Goals (SDGs). By decoupling chemical recovery from fossil thermal energy, electrified bioseparations accelerate progress toward SDG 7 (Affordable and Clean Energy) and SDG 13 (Climate Action). Furthermore, replacing stoichiometric chemical precipitation—which generates hazardous solvent waste and mineral sludges—with non-thermal, reagent-free electromigration directly supports SDG 12 (Responsible Consumption and Production). Finally, the capacity of EDMs to recover mineral nutrients (NH_4^+ , PO_4^{3-}) and clean water from high-strength industrial effluents contributes significantly to SDG 6 (Clean Water and Sanitation), establishing these platforms as foundational tools for circular bioeconomies.

6.3. Dynamic Integration with Intermittent Renewable Grids

The most profound strategic advantage of electro-driven separations over thermal systems is their lack of thermal inertia. A distillation column requires hours to reach steady-state temperatures and cannot be easily ramped up or down. In contrast, electro-membrane systems possess near-instantaneous response times, making them uniquely capable of operating as flexible electrical loads [55,57,136].

As global electrical grids transition toward intermittent renewable sources (solar and wind), periods of massive energy overgeneration (negative electricity pricing) and severe shortages are becoming common. Electro-driven bioseparations can dynamically modulate

their applied voltage or current density in real time to match grid availability. During periods of surplus renewable generation, the system can aggressively ramp up current density to maximize extraction; during peak grid demand, the system can dial back to a maintenance voltage.

Engineering Trade-offs and Operational Constraints: While dynamic, load-following operation provides distinct energy-cost advantages, subjecting an operating electro-membrane stack to frequent current density fluctuations introduces specific physicochemical challenges. Rapid voltage ramping can induce transient imbalances in concentration polarization boundary layers, destabilize localized interfacial pH, and inflict mechanical stress on electroactive polymer polymers through continuous redox cycling. To ensure long-term reliability under variable power inputs, research must move beyond treating the membrane stack as a simple variable resistor. Systems engineering must focus on developing transient-resilient polymer architectures and predictive digital-twin control algorithms capable of maintaining stable permselectivity and current efficiency during rapid operational shifts.

6.4. Techno-Economic Realities: CapEx vs. OpEx and System Boundaries

The industrial deployment of electro-driven systems depends strictly on comprehensive Techno-Economic Analysis (TEA) [11]. The commercial viability of an EDMS is strongly influenced by the market value of the target biochemical. High-value nutraceuticals and specialty pharmaceutical intermediates can absorb the higher CapEx associated with advanced, nano-engineered 2D or MOF membranes. However, recovering bulk commodity chemicals (e.g., acetic acid, bulk biofuels, or mineral fertilizers) demands low OpEx and scalable, low-cost membrane modules to compete with established petrochemical production costs.

For electro-separations, OpEx is largely dominated by electricity costs and membrane replacement. The degradation of the membrane—whether through irreversible biofouling, binder dissolution, or anodic oxidation—simultaneously inflates the electrical resistance (driving up energy costs) and necessitates frequent physical replacement.

To prevent discrepancies in economic reporting, future TEA and LCA evaluations must establish standardized, comprehensive system boundaries. Analyses can no longer evaluate the electro-membrane stack in isolation. A standardized TEA system boundary must explicitly incorporate: (1) primary solid-liquid separation and pre-treatment filtration (e.g., ultrafiltration or microfiltration); (2) fluid pumping and recirculation energetics across all stack manifolds; (3) chemical consumption and waste treatment associated with clean-in-place (CIP) protocols; (4) empirical membrane replacement schedules based on real-world long-term degradation rates; and (5) downstream polishing required to achieve a standardized functional unit ($\text{kWh}/\text{kg}_{\text{product}}$ at a defined commercial purity, e.g., >95%).

Consequently, the most significant economic leverage of electro-driven systems does not come from isolating a single product slightly cheaper. It comes from process intensification: utilizing a single bipolar membrane system to simultaneously recover a target acid, recycle nutrients, generate in situ buffering capacity, and eliminate the need for six separate downstream chemical dosing and filtration tanks. Future TEA frameworks must abandon unit-to-unit comparisons and evaluate the total economic impact of electro-driven flow-sheet simplification on the CapEx and OpEx of the entire biorefinery.

6.5. Quantitative Case Study: Benchmarking Energetics, Emissions, and Economics

To transition from theoretical thermodynamics to industrial reality, this section synthesizes empirical data from recent state-of-the-art electro-membrane systems to quantify the multidimensional tradeoffs governing specific energy consumption (SEC), carbon foot-

print, and operating expenditure (OpEx). The benchmarked systems focus on recovering high-volume, challenging targets: nutrients (ammoniacal nitrogen) from human urine and digestate, and carboxylic acids (caproic acid and mixed volatile fatty acids) from complex fermentation broths.

6.5.1. System-Level Energetics and the Flux-SEC Tradeoff

The inescapable inverse thermodynamic relationship between volumetric productivity (flux) and energy efficiency is rigorously demonstrated across multiple targeted biochemicals. For instance, in the recovery of caproic acid via bipolar membrane electrodialysis (BMED), Zhao et al. [203] applied a highly aggressive current density of 200 A/m². This intense driving force successfully concentrated the acid past its aqueous solubility limit (10.82 g/L), inducing spontaneous liquid–liquid phase separation to yield an oily product layer with 82.58% purity. However, this productivity came at a severe thermodynamic cost: the Ohmic dissipation and water dissociation penalties drove the specific energy consumption to 7.57 kWh/kg of total extracted carboxylic acid [203]. This energy penalty is even more pronounced during the extraction of dilute nitrogen.

A novel four-chamber electrochemical membrane system (4C-EMS) processing complex digester centrate achieved an exceptional SEC of 8.2 ± 0.2 kWh/kg N when operating at a conservative current density of 1.25 mA/cm² [204]. However, when operators attempted to maximize flux by aggressively scaling the current density up to 10 mA/cm², the SEC nearly quadrupled to 29.5 ± 0.6 kWh/kg N due to severe concentration polarization and parasitic voltage losses at the membrane boundary layers [204]. Similarly, an electrified ion-exchange stripping (EXS) process recovering nitrogen from source-separated urine reported tunable, highly divergent SECs ranging from 27.7 to 83.3 kWh/kg N, strictly dictated by the engineered conductivity of the supporting electrolyte [191]. These empirical data unequivocally validate the argument established in Section 6.1: engineering optimization must pursue machine learning-driven Pareto fronts rather than targeting isolated, brute-force maxima in membrane flux.

6.5.2. Carbon Footprint Benchmarking: The Grid-Dependence of Electrification

As argued in Section 6.2, the true decarbonization potential of electro-driven separations is strictly governed by the carbon intensity of the regional electrical grid. Translating these empirical SEC values into Scope 2 lifecycle emissions reveals a heavily bifurcated environmental reality:

- **Fossil-Dominant Grid Scenario (≈ 1.0 kg_{CO_{2e}}/kWh):** Driving the BMED extraction of caproic acid at 7.57 kWh/kg results in a massive embodied footprint of 7.57 kg_{CO_{2e}}/kg_{product} [203]. Similarly, nitrogen recovery via the 4C-EMS at 1.25 mA/cm² emits 8.2 kg_{CO_{2e}}/kg N [204]. Under these fossil-heavy conditions, the electro-membrane system simply shifts the emissions upstream to the power plant, offering negligible climate mitigation compared to a conventional, natural-gas-fired thermal evaporator.
- **Renewable-Dominant Grid Scenario (≈ 0.1 kg_{CO_{2e}}/kWh):** Conversely, sourcing the identical electrical work from decarbonized grids (e.g., wind or solar) collapses the emissions footprint of caproic acid recovery to a highly sustainable 0.75 kg_{CO_{2e}}/kg_{product} [203]. The footprint for nitrogen extraction identically plummets to a mere 0.82 kg_{CO_{2e}}/kg N [204].

These hard metrics demonstrate that without dynamic integration with renewable power generation, the simple act of process electrification does not intrinsically guarantee a “green” pathway.

6.5.3. Techno-Economic Analysis (TEA) and Process Intensification

The industrial deployment of these systems hinges strictly upon minimizing OpEx—dominated by bulk electricity and external chemical dosing—relative to the commodity market value of the target biochemical. For example, Liu et al. [204] estimated the total operational cost of the 4C-EMS for ammonia recovery at \$0.58 to \$0.83/kg N. This narrow margin is highly competitive with the bulk petrochemical market price of ammonia ($\approx$ \$0.74/kg N) [204]. Crucially, this economic threshold was only achieved through process intensification: the system inherently produced acid via anodic water electrolysis, offsetting 10–32% of the exogenous acid typically required for downstream ammonia absorption. Without this in situ generation, the cost of external chemical buffers would fatally inflate the OpEx.

In volatile fatty acid (VFA) recovery, integrating BMED takes this economic concept to its logical extreme by bypassing downstream chemical purchasing entirely. Treating a complex fermentation broth peaking at 8.20 g/L of VFAs, a continuous BMED unit utilized water dissociation to simultaneously yield both an acidified, concentrated VFA product stream and a continuous, high-purity alkali regenerate [86]. Operating at an optimal current density of 30 mA/cm², the system maintained efficient hydroxide flux while consuming a mere 0.68 kWh over a 24-h batch cycle [86]. By routing this electro-generated alkali directly back into the live fermenter for continuous pH stabilization, the system entirely eliminated the OpEx drain of purchasing exogenous sodium hydroxide. Ultimately, these case studies prove that the techno-economic viability of electro-driven separations does not stem from isolated membrane performance; it stems directly from flowsheet consolidation—replacing multiple distinct unit operations, thermal evaporators, and chemical dosing tanks with a single, highly integrated cyber-physical membrane stack.

Table 5. Comparative Thermodynamics, Sustainability, and Techno-Economic Benchmarks of Bioseparation Pathways.

Performance Indicator	Electro-Driven Membrane Separations	Thermal Separations (Distillation/Evaporation)	Chemical-Based Separations (Precipitation/Solvent Extraction)	Critical Perspective/Industrial Implication
Thermodynamic Driving Force	Programmable electric potential gradients, localized proton flux, and speciation modulation.	Latent heat of vaporization (ΔH_{vap}) acting indiscriminately upon the bulk solvent.	Stoichiometric chemical potential via the exogenous dosing of acids, bases, or organic solvents.	Paradigm Shift: Electrification physically decouples the separation energy from the bulk water volume, directing electrical work exclusively toward the target molecule.
Energy Scaling and Specific Energy Consumption (SEC)	Scales with target mass (0.5–7.5 kWh/kg). Highly advantageous for processing dilute (<5 wt%) fermentation broths.	Scales massively with bulk water volume. Extreme thermodynamic penalty when treating dilute biorefinery streams.	Energy footprint is embedded within the lifecycle manufacture and transport of the massive reagent volumes required.	The Dilution Paradox: Electro-separations excel in dilute streams, but SEC spikes exponentially if highly mobile background salts in the broth monopolize the applied current.
Molecular Discrimination and Purity Limits	High. Governed by interfacial Donnan exclusion, sub-nanometer steric gating, and isoelectric point trapping.	Limited entirely by relative volatility (α) and azeotrope formation. Cannot distinguish heavy structural isomers.	Variable. Governed by partition coefficients, complexation affinity, and strictly pH-dependent solubility limits.	Isomeric Precision: Electrified interfaces enable the precise fractionation of zwitterions and homologous organic acids that are thermally and chemically indistinguishable.
Process Intensification and Bioreactor Integration	Exceptional. Enables continuous in situ product recovery and real-time pH buffering without harming live biomass.	Strictly sequential/downstream. The application of latent heat is fundamentally lethal to live microbial cultures.	Batch-limited by massive volumetric dosing, reaction settling times, and extreme pH shocks to the broth.	Flowsheet Consolidation: Electro-systems transition the membrane from a passive downstream filter into an active cyber-physical regulator of the live fermentation loop.

Table 5. Cont.

Performance Indicator	Electro-Driven Membrane Separations	Thermal Separations (Distillation/Evaporation)	Chemical-Based Separations (Precipitation/Solvent Extraction)	Critical Perspective/Industrial Implication
Lifecycle Carbon and Environmental Footprint	Zero exogenous dosing. Scope 2 emissions are strictly dictated by the carbon intensity of the regional electrical grid.	Massive Scope 1 emissions generated directly on-site via continuous fossil-fired boilers and steam generation.	Generates massive stoichiometric solid waste (e.g., gypsum from calcium-lactic acid precipitation) and toxic solvent sludge.	The Grid Dependency: Without dynamic integration with decarbonized renewable grids (wind/solar), electro-separations merely shift greenhouse gas emissions upstream.
Techno-Economic Bottlenecks (CapEx/OpEx)	CapEx: High (membrane/stack area). OpEx: Dominated by electricity and cyclic membrane replacement.	CapEx: High (exotic, corrosion-resistant metallurgy). OpEx: Dominated by continuous natural gas procurement.	CapEx: Moderate (mixing/settling tanks). OpEx: Dominated by reagent procurement and toxic waste disposal fees.	The Economic Tipping Point: The commercial competitiveness of electro-separations hinges entirely on maximizing membrane lifespan against biofouling and anodic oxidation.
Industrial Maturity and Primary Failure Modes	TRL 4–7 (for bioseparations). Fails via irreversible EPS biofouling, internal inorganic scaling, and Faradaic oxidation.	TRL 9 (Commercially mature). Fails via severe inorganic scaling, extreme thermal degradation, and corrosion.	TRL 9 (Commercially mature). Fails via solvent degradation, stable emulsion formation, and reagent crossover.	The Innovation Mandate: While thermally mature, legacy methods are environmentally obsolete for circular bioeconomies. Scaling electro-membrane technology requires resolving severe bio-incompatibilities.

7. Reliability, Stability, and Scale-Up Challenges

Despite remarkable advances in programmable selectivity and interfacial nano-engineering, the industrial commercialization of electro-driven bioseparations remains severely crippled by a lack of long-term operational reliability. The literature is oversaturated with reports of unprecedented permselectivity and near-perfect energy metrics, yet these data are almost universally derived from short-duration (e.g., 24–48 h) laboratory experiments utilizing pristine, synthetic model solutions [1,41,70,136,145]. These idealized metrics fail completely when subjected to the harsh realities of an industrial biorefinery, where a membrane stack must operate continuously for 8000 h per year while processing chemically chaotic, rheologically viscous, and biologically active fluids.

Under authentic operational conditions, the permselectivity of a membrane ceases to be an intrinsic material property. Instead, performance is dictated by the compounding, macro-scale failure cascade of irreversible biofouling, aggressive electrochemical degradation, and severe hydrodynamic maldistribution within the stack. As conceptualized in Figure 5, catastrophic membrane failure in electro-driven systems is rarely the result of a single mechanism; it is the synergistic collapse of the material architecture, the electrical field distribution, and the fluid dynamics.

To transition from empirical observation to predictive engineering, reliability must be evaluated through standardized, objective degradation indicators. Evaluating an EDMS requires monitoring: (1) *SEC drift* ($\Delta\text{SEC}/\Delta t$), which quantifies the progressive increase in energy required to transport a unit mass of product due to membrane scaling or polarization; (2) *Ohmic resistance increase*, measured via real-time in situ Electrochemical Impedance Spectroscopy (EIS); (3) *ion-exchange capacity (IEC) retention*, which indicates the preservation of fixed surface charge groups; (4) *permselectivity decay* over extended biological exposure; and (5) *clean-in-place (CIP) frequency*, which dictates module maintenance downtime and operational lifecycle costs.

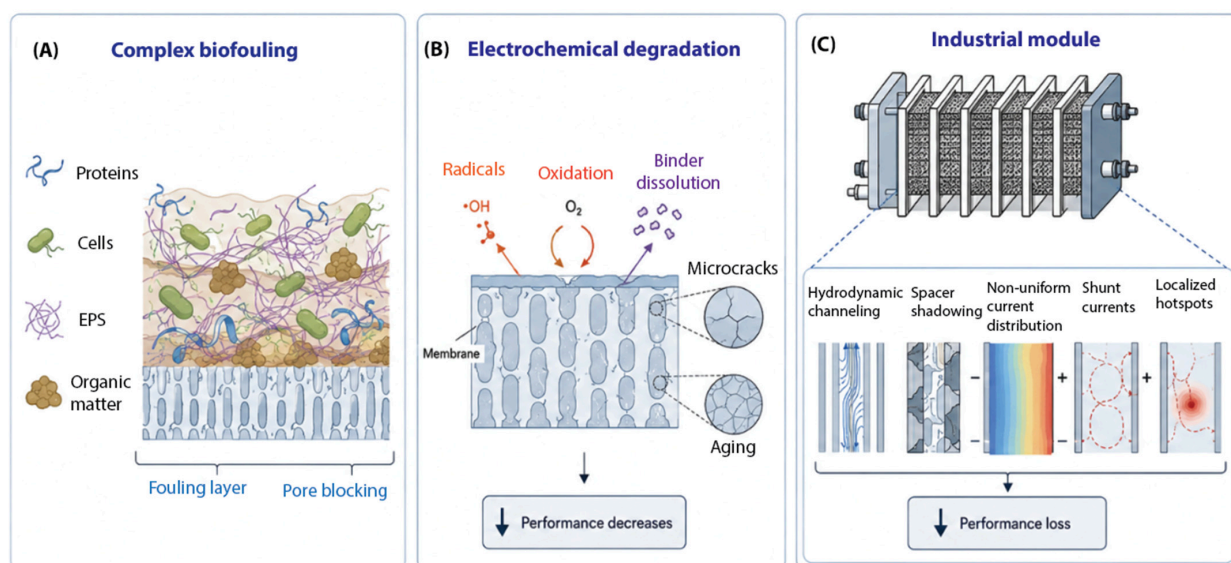


Figure 5. The critical system failure cascade in industrial electro-separations. Sustained permselectivity is ultimately destroyed by the synergistic coupling of (A) electro-biologically driven fouling and irreversible EPS gelation at the boundary layer; (B) aggressive electrochemical degradation via localized radical attack, anodic oxidation, and polymer binder dissolution; and (C) module-scale electro-hydrodynamic maldistribution, characterized by parasitic shunt currents, spacer shadowing, and localized Joule heating.

7.1. Complex Fouling Dynamics in Biostreams and Mitigation Strategies

Fouling in electro-driven bioseparations is fundamentally more aggressive than the passive scaling observed in pressure-driven desalination (e.g., reverse osmosis). In biorefinery effluents, the membrane is subjected to a dense cocktail of amphiphilic proteins, extracellular polymeric substances (EPS), lipid bilayers, and cellular debris [59,163,173,175]. Crucially, in an electro-driven system, these bio-macromolecules are not merely passively transported by fluid convection; they are forcefully electro-migrated directly into the interfacial electrical double layer. Once driven into the interface, the severe localized pH extremes—caused by concentration polarization and water dissociation at the boundary layer—trigger immediate protein denaturation and isoelectric precipitation. The denatured proteins irreversibly bind to the membrane surface via hydrophobic and electrostatic interactions, forming a highly cohesive, gel-like conditioning layer.

This biological scaffold subsequently entraps migrating multivalent cations (Ca^{2+} , Mg^{2+}) and organic acid anions, catalyzing localized organic–inorganic co-precipitation. The consequences of this electro-biologically coupled fouling are devastating to the system's thermodynamics. The EPS gel layer radically alters the dielectric constant of the interface and acts as a massive electrical insulator. To maintain the target molecular flux, operators must exponentially increase the applied voltage, immediately destroying the specific energy consumption (kWh/kg) of the separation.

To systematically address these complex interactions, Table 6 categorizes the primary fouling mechanisms encountered in EDMS bioseparations, pairing each specific failure mode with proven engineering and architectural mitigations.

Engineering Trade-offs and Operational Constraints: The membrane science community frequently evaluates anti-fouling efficacy by measuring hydraulic flux preservation or visual reductions in surface deposition. In electro-driven membrane systems, however, hydraulic permeability alone is an incomplete indicator of performance. A membrane may maintain constant fluid permeability while accumulating a thin, electrochemically insulating monolayer of denatured protein or EPS. This organic boundary layer can mask

fixed surface charges, alter local dielectric constants, and increase transmembrane Ohmic resistance, leading to a decay in permselectivity and an increase in specific energy consumption (kWh/kg). Consequently, industrial benchmarking of anti-fouling architectures should move beyond simple flux-decline models and evaluate performance through the long-term preservation of molecular selectivity, current efficiency, and SEC stability during extended operation in authentic biological broths.

Table 6. Systematic classification of fouling mechanisms in electro-driven bioseparations and paired engineering mitigations.

Fouling Classification	Dominant Foulant Species	Primary Physical and Thermodynamic Mechanism	Impact on System Performance Indicators	Paired Engineering and Architectural Mitigations
1. Organic Adsorption	Amphiphilic proteins, lipids, hydrophobic metabolites.	Electrostatic tethering and hydrophobic interactions driven by boundary-layer polarization.	Forms insulating monolayers; alters interfacial dielectric constant; increases transmembrane Ohmic resistance.	• Surface Engineering: Grafting zwitterionic polymer brushes or hydrophilic coatings (e.g., PEG, polyvinyl alcohol) to increase hydration energy barriers. • Operational: Sub-isoelectric boundary-layer pH buffering.
2. Biofouling	Extracellular polymeric substances (EPS), microbial cells, cellular debris.	Electro-migration of negatively charged colloids into the EDL, forming dense gel layers.	Causes severe concentration polarization; blinds fixed-charge groups; increases SEC drift ($\Delta\text{SEC}/\Delta t$).	• Operational: Asymmetric pulsed-reversed polarity (PRP) to electrostatically repel bio-colloids. • Pre-treatment: Zero-shear microfiltration or inline UV/enzymatic EPS disruption.
3. Inorganic Scaling	Multivalent cations (Ca^{2+} , Mg^{2+}), carbonates, phosphates.	Alkaline boundary-layer pH shifts (due to water splitting) inducing localized crystal nucleation.	Blinds ion-exchange sites; physically damages polymer matrices via internal crystal growth; reduces current efficiency (η).	• Material: Deploying strictly monovalent-selective permselective coatings. • Operational: Limiting current density control to prevent interfacial water dissociation; periodic acid washing.
4. Electrochemical Fouling	Electroactive organics, phenolic compounds, unsaturated fatty acids.	Faradaic oxidation or reduction at polarized conductive membrane/electrode interfaces.	Forms impermeable, electronically insulating polymeric films directly on active surfaces; degrades electrode capacitance.	• Material: Utilizing non-catalytic, pseudo-capacitive transition metal coatings. • Operational: Maintaining cell potentials below specific organic redox thresholds (<1.2 V).
5. Mixed-Matrix Co-Precipitation	Organic acids trapped within inorganic mineral frameworks (e.g., calcium-lactate complexes).	Synergistic coupling of gel-layer formation with multivalent mineral entrapment.	Severe flux collapse; permanent loss of permselectivity; mechanical delamination of thin-film composite layers.	• Hydrodynamic: 3D-printed fractal spacers to eliminate stagnant boundary-layer shadowing. • System: Continuous in situ crystallization loops to deplete multivalent cations upstream.

7.2. Electrochemical and Chemical Degradation

Electro-driven membranes are not passive physical barriers; they are structural polymers immersed in a highly reactive, localized battery cell [12,188]. While pressure-driven membranes degrade primarily via mechanical compaction or chlorine exposure, electrified interfaces are systematically destroyed by the extreme electrochemical microenvironments they generate. When an electro-membrane operates near or above its limiting current

density, severe water dissociation ($\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$) occurs at the depleted boundary layer. This subjects the membrane surface to localized pH values approaching 1.0 on one face and 14.0 on the opposite face, regardless of the bulk fluid pH.

Under continuous exposure to these extreme localized gradients, the delicate functional groups responsible for ion exchange—particularly the quaternary ammonium groups in anion exchange membranes—undergo rapid, irreversible nucleophilic substitution and Hofmann elimination. As these fixed-charge groups are cleaved from the polymer backbone, the membrane permanently loses its ion-exchange capacity (IEC) and permselectivity.

Furthermore, the integration of advanced conductive matrices (e.g., MXenes, CNTs) introduces severe vulnerabilities to anodic oxidation. Trace parasitic oxygen evolution at the anode generates highly reactive hydroxyl radicals ($\text{OH}^\bullet$) and peroxide intermediates. These radical species aggressively attack the carbonaceous matrices and the underlying polymer binders (e.g., PVDF, PTFE). Over repeated charging cycles, this radical attack physically disintegrates the conductive network, causing the membrane to delaminate, shed its catalytic nanoparticles directly into the biological product stream, and completely lose its electro-responsive capabilities.

To establish industrial reliability, material performance claims must be supported by standardized, multi-parameter chemical and electrochemical stability protocols. Evaluating next-generation EDMS architectures requires: (1) long-term chronoamperometry under sustained limiting current density conditions (>500 h); (2) accelerated radical exposure assays, subjecting membranes to in situ Fenton-type reagent stress ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) to quantify oxidative degradation resistance; (3) continuous voltage cycling across relevant operational potentials to evaluate mechanical fatigue and binder stability; (4) post-operational IEC quantification via titration to calculate fixed-charge loss rates; and (5) structural characterization using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) to verify surface chemical integrity and detect micro-cracking.

Engineering Trade-offs and Operational Constraints: Incorporating highly functionalized 2D nanomaterials into electro-separations offers distinct interfacial selectivity advantages; however, their long-term stability under industrial voltage cycling requires thorough evaluation. A high-initial-selectivity membrane that experiences rapid IEC decay or polymer binder dissolution after limited operational cycling (<100 h) presents significant replacement costs that impact OpEx. Advancing novel membrane chemistry toward commercial relevance demands adopting accelerated electrochemical aging protocols (AEP), validating material longevity under sustained current overloads and radical exposure prior to industrial scaling.

7.3. Engineering Module Scale-Up Realities

Translating high permselectivity observed in small laboratory membrane coupons ($\approx 10 \text{ cm}^2$) to industrial modules containing large membrane areas (>100 m^2) requires overcoming macroscopic engineering constraints. As physical stack dimensions increase, separation physics transitions from being material-limited to being increasingly governed by hydrodynamic and electrical distribution across the module [205,206]. In industrial-scale electrodialysis stacks, fluid maldistribution can occur. Standard spacer meshes—designed to promote mixing—can create localized low-velocity zones where fluid velocity approaches zero.

These low-velocity regions experience rapid, localized concentration polarization. Because electrical current follows the path of least resistance, current bypasses these polarized, high-resistance zones and concentrates in high-velocity, clean areas of the membrane. This localized current focusing generates non-uniform current distribution, inducing localized Joule heating, thermal polymer stress, and potential membrane burn-through.

Furthermore, as the number of cell pairs in an industrial stack increases, parasitic shunt currents become an important energy penalty. In large stacks, highly conductive biological fluid within common distribution manifolds provides an alternative electrical pathway. Instead of driving target molecules across transmembrane interfaces, up to 10–20% of applied electrical power can bypass cell pairs entirely, short-circuiting through the manifold. This increases specific energy consumption and disrupts electric field uniformity across the module.

Engineering Trade-offs and Operational Constraints: While fundamental membrane research focuses on tuning sub-nanometer free volume and interfacial charge, industrial scale-up is heavily governed by meter-scale fluid dynamics and electrical stack engineering [207,208]. An electro-driven bioseparation system functions as a multi-scale electrochemical reactor. Overcoming scale-up bottlenecks requires integrating materials science with module-level mechanical engineering—specifically deploying 3D-printed, computationally optimized fractal spacers to eliminate stagnant shadowing, utilizing computational fluid dynamics (CFD) coupled with primary current distribution modeling, and redesigning manifold geometries to suppress shunt currents and enforce uniform electro-hydrodynamic conditions across large-scale assemblies.

8. Toward Intelligent and Industrially Integrated Electro-Driven Biorefineries

The evolution of electro-driven membrane technologies is approaching a critical industrial threshold: the transition from the isolated optimization of individual membrane coupons to the deployment of fully integrated, electrified biorefineries. Historically, the biochemical industry has treated downstream processing as an independent, sequential penalty—a rigid unit operation bolted onto the end of a fermenter. This highly compartmentalized architecture inherently multiplies capital investment, inflates energy consumption, and generates massive chemical waste.

The next generation of sustainable biomanufacturing demands a total paradigm shift. Biological conversion, electrochemical extraction, in situ buffering, and nutrient recycling must cease to be separate steps; they must operate simultaneously as interconnected thermodynamic loops within a unified cyber-physical system [2,7,209]. Within this emerging framework, electrified membranes transcend their traditional role as mere selective barriers. They become active, programmable molecular interfaces capable of regulating chemical gradients, dynamically responding to shifting microbial metabolism, and closing circular mass balances.

8.1. Standardized Testing Protocols and Benchmarking Guidelines

To accelerate industrial translation and enable meaningful cross-literature comparison, the electro-membrane community must establish standardized benchmarking protocols. Currently, empirical reporting is highly fragmented: experimental duration, feed composition, and energy calculations vary widely across published studies. To bridge the gap between academic innovation and commercial deployment, future investigations evaluating EDMS for bio-based chemical recovery should adhere to five mandatory benchmarking criteria:

1. **Realistic Feed Matrices:** Proof-of-concept experiments in binary synthetic solutions (e.g., target acid in pure NaCl) must be complemented by validation in authentic or high-fidelity simulated industrial matrices. Reporting must specify background inorganic salt concentrations (K^+ , Cl^- , PO_4^{3-}), total dissolved solids (TDS), chemical oxygen demand (COD), and initial pH.

2. **Explicit Membrane Characterization:** Studies must report standardized physical and electrochemical properties of the membrane prior to and following operation, including dry/wet thickness (μm), ion-exchange capacity ($\text{mmol/g}_{\text{dry}}$), electrical resistance ($\Omega \text{ cm}^2$) measured in a standardized electrolyte (0.5 M NaCl at 25 °C), and effective membrane surface area (cm^2 or m^2).
3. **Comprehensive Electrochemical Reporting:** Operational driving forces must be defined explicitly. Authors must report current density (mA/cm^2), cell voltage (V), transmembrane potential difference, and Faradaic current efficiency ($\eta\%$). For systems utilizing periodic polarity reversal or pulsing, pulse duration, frequency, and duty cycle must be fully documented.
4. **Normalized Energy and Productivity Metrics:** System performance must be evaluated using standardized functional units. Volumetric productivity must be reported as $\text{g}_{\text{product}}/\text{m}^2/\text{h}$. Specific Energy Consumption (SEC) must be calculated in $\text{kWh/kg}_{\text{product}}$ and explicitly state whether the energy boundary includes only stack DC power or incorporates auxiliary pumping and pre-treatment energetics.
5. **Long-Term Durability and Reliability Tracking:** To validate operational stability, continuous testing durations must extend beyond initial 24-h screens. Benchmarking protocols should target a minimum continuous operating window of 100–500 h in real biological broths, documenting SEC drift ($\Delta\text{SEC}/\Delta t$), permselectivity decay, and required clean-in-place (CIP) frequency.

8.2. The Fully Electrified Biorefinery Vision and Closed-Loop Constraints

The electrified biorefinery represents an important operational shift in chemical manufacturing. Conventional biorefining requires that carbon fixed by microbes is subsequently subjected to fossil-fueled thermal separation and caustic chemical conditioning [7]. This approach limits the environmental value proposition of the bioeconomy. The fully electrified biorefinery addresses this limitation by replacing legacy evaporation, precipitation, and solvent extraction with targeted electromigration, decoupling downstream processing from latent heat and bulk phase changes. The facility can be powered by low-carbon or renewable electricity. Furthermore, this architecture modifies linear waste streams; dilute organic carbon, volatile fatty acids, and mineral nutrients (N, P) previously discarded to wastewater treatment are concentrated via electro-separation and routed back to the bioreactor loop.

Engineering Trade-offs and Operational Constraints: While electrifying a biorefinery offers theoretical sustainability benefits [210,211], achieving net-positive environmental impact depends strictly on the carbon intensity of the regional electrical grid ($\text{kg CO}_2 \text{ eq/kWh}$). Furthermore, replacing robust thermal infrastructure with electro-membrane stacks introduces operational sensitivities regarding membrane fouling and degradation.

Most critically, implementing continuous, closed-loop fluid recycling introduces a specific thermodynamic challenge: contaminant accumulation. When residual effluents are continuously concentrated and recirculated to the fermenter, non-target species—including heavy metal trace ions (Cu^{2+} , Zn^{2+}), non-metabolizable residual sugars, cell-lysis byproducts, and inorganic salts (Cl^- , SO_4^{2-})—accumulate within the loop. If the rate of recirculation exceeds the metabolic assimilation capacity of the microbial culture, these species reach inhibitory thresholds, inducing hyper-osmotically driven cellular dehydration, enzyme inhibition, and fermentation stall. To maintain closed-loop stability, integrated flowsheets must incorporate selective purge streams or specialized nanofiltration/capacitive deionization kidney loops designed to selectively reject and bleed non-target trace contaminants while retaining vital carbon and nutrients.

8.3. AI-Guided Material Discovery and Digital-Twin Process Modeling

The physical mechanisms governing electro-driven bioseparations—including boundary-layer fluid dynamics, non-equilibrium electrostatics, dynamic speciation, and localized pH shifts—create a multidimensional design space that is challenging to optimize using empirical trial-and-error alone. Historically, membrane fabrication and process optimization have relied on iterative screening: synthesizing a polymer, measuring bulk flux, and incrementally adjusting monomer ratios. To navigate the thermodynamic trade-offs detailed in Section 6, machine learning (ML) and artificial intelligence (AI) methodologies are increasingly being integrated into membrane science.

By coupling ML algorithms with high-throughput Molecular Dynamics (MD) simulations, researchers can computationally screen structural configurations of Covalent Organic Frameworks (COFs), MXenes, and polymeric composites. Predictive algorithms can evaluate how pore geometry, surface electronegativity, and functional group distribution influence permselectivity for target biochemicals prior to laboratory synthesis. At the system level, implementing robust “Digital Twins” in industrial biomanufacturing requires bridging the gap between theoretical modeling and physical hardware integration. An operational digital twin for an EDMS requires three synchronized layers:

1. **Multi-Physics Solver Engine:** The core mathematical model must continuously solve the coupled extended Nernst–Planck, Donnan equilibrium, and Poisson equations across finite-volume stack geometries, dynamically updating effective ionic mobility based on Henderson–Hasselbalch acid dissociation (pKa) and temperature.
2. **Real-Time Sensor Integration:** The physical stack must transmit synchronized, high-frequency online data streams to the digital twin, specifically incorporating: (a) in situ multi-frequency Electrochemical Impedance Spectroscopy (EIS) to monitor boundary-layer Ohmic resistance and detect early-stage biofilm nucleation; (b) inline optical refractive index and conductivity sensors to measure real-time ion flux; and (c) boundary-layer pH electrodes located at module inlet and outlet manifolds.
3. **Autonomous Control Actuators:** The predictive output of the digital twin must directly manipulate physical control variables, dynamically adjusting applied current density, cross-flow fluid velocity, and asymmetric pulse-reversal frequency to maintain operation within the optimal Pareto efficiency frontier.

Engineering Trade-offs and Operational Constraints: The current application of AI in membrane science faces limitations regarding training data quality and diversity. Machine learning models are heavily dependent on the datasets they ingest. Currently, published literature is predominantly composed of data derived from short-duration experiments using simple synthetic salt solutions under steady-state conditions. An algorithm trained exclusively on pristine aqueous electrolyte data cannot reliably predict complex fouling kinetics or competitive transport in an extracellular-polymeric-substance-laden fermentation broth. Advancing AI from a theoretical modeling technique to a reliable industrial tool requires generating standardized, high-fidelity experimental databases that document matrix effects, long-term degradation kinetics, and negative operational results obtained from authentic industrial feedstocks. To transition from conceptual modeling to industrial implementation, the integration of intelligence into electro-separations must follow a structured developmental roadmap:

1. **Demonstrated Current Capability (TRL 3–5):** Offline machine-learning screening of membrane materials and static Computational Fluid Dynamics (CFD) stack modeling using historical baseline data.

2. **Near-Term Research Need (TRL 5–6):** Integrating real-time in situ Electrochemical Impedance Spectroscopy (EIS) and optical sensors with automated control actuators to execute adaptive voltage throttling and pulse-reversal during early-stage fouling.
3. **Long-Term Development Vision (TRL 7–9):** Fully autonomous, self-optimizing digital twins that continuously solve multi-physics reactive-transport equations in real time, dynamically coupling membrane driving forces to live, fluctuating bioreactor loops under variable renewable grid pricing.

8.4. Smart and Autonomous Electro-Separations

Many conventional electro-membrane systems operate on static set-points—applying a constant voltage or current density regardless of dynamically changing conditions inside the bioreactor [12,85,203]. Static control can be sub-optimal for biological feeds; as fermentation progresses, broth viscosity increases, background salinity shifts, and target molecule isoelectric points adapt to metabolic byproducts. To optimize efficiency, systems must transition toward dynamic, autonomous cyber-physical control.

This transition relies on integrating real-time in situ sensors, particularly Electrochemical Impedance Spectroscopy (EIS). Continuous EIS monitoring allows the system to detect early-stage organic deposition or mineral scaling by identifying characteristic impedance shifts across the membrane interface.

Utilizing this real-time data, autonomous control algorithms can execute automated operational adjustments. If impedance signatures indicate the onset of severe concentration polarization, the system can autonomously reduce applied current density. If organic protein fouling is detected, the stack can trigger a high-frequency, asymmetric reversed-polarity pulse to dislodge foulants before structural consolidation occurs. This integration enables the membrane stack to function as an adaptive, self-regulating unit operation.

Engineering Trade-offs and Operational Constraints: The primary challenge in implementing autonomous electro-separations lies in hardware durability rather than control software. Advanced algorithms that command high-frequency voltage pulsing or rapid polarity reversal subject the membrane stack to cyclic electromechanical stress. Rapidly alternating the electric field can induce localized osmotic swelling and contraction within the polymer matrix, which over time can lead to micro-cracking, delamination of thin-film composite layers, and accelerated degradation of dimensionally stable anodes (DSAs). Achieving long-term autonomous control requires materials engineering focused on developing mechanical-fatigue-resistant polymer supports and robust electrode coatings capable of surviving extended high-frequency voltage cycling without structural degradation.

8.5. Grand Challenges and the Industrial Mandate

Electro-driven membrane separations have demonstrated the capacity to manipulate molecular transport with angstrom-scale precision. However, translating laboratory discoveries into commercial biorefinery operations requires addressing specific engineering and materials challenges. Moving forward, research efforts should prioritize the following strategic mandates:

1. **Transition to Authentic Feed Matrices:** The evaluation of bioseparation membranes exclusively in binary synthetic solutions should be phased out. Research programs must prioritize validating materials and modules in raw or pre-treated industrial fermentates to accurately quantify competitive co-ion transport, organic matrix effects, and authentic biofouling dynamics.
2. **Mandatory Thermodynamic Accounting:** Reporting high permselectivity or volumetric flux without accounting for energy consumption provides an incomplete assessment of viability. Investigations should report Specific Energy Consump-

tion (kWh/kg_{product} across defined system boundaries and benchmark performance against the thermal or chemical baseline the technology aims to displace.

3. **Scalable Roll-to-Roll (R2R) Manufacturing:** Advanced 2D laminates (MXenes, COFs) and nanostructured membranes must transition from complex lab-scale synthesis to scalable manufacturing methods. Research should emphasize roll-to-roll (R2R) casting, interfacial polymerization, and green solvent processing to produce square-meter modules with uniform electrical and structural properties.
4. **Holistic Bioreactor-Loop Integration:** Membrane modules must be designed for biophysical compatibility with live fermentation loops. System optimization should balance extraction efficiency against cellular shear stress, electroporation limits, and trace-mineral retention to maintain long-term microbial viability.

Electro-driven membranes represent programmable electrochemical platforms capable of advancing circular bioeconomies. By integrating materials science, electrochemical engineering, and digital process control, this technology has the potential to transform downstream processing from an energy-intensive purification bottleneck into an adaptive platform for resource recovery. Realizing the integrated electro-biorefinery requires systematically addressing the engineering challenges that govern commercial scale-up. Table 7 synthesizes the primary knowledge gaps facing the field and outlines actionable research mandates necessary to transition electro-driven bioseparations from laboratory concepts to industrial implementations.

Table 7. Strategic roadmap, analytical knowledge gaps, and actionable engineering mandates for the industrialization of electro-driven biorefineries.

Strategic Research Domain	Identified Knowledge Gap and Scaling Bottleneck	Current Technological Limitation (Status Quo)	Actionable Engineering and Research Mandate	Target Industrial Impact (TRL 7–9)
1. Multicomponent Transport Thermodynamics	Static-Charge Assumptions vs. Dynamic Speciation: Theoretical models rely on static bulk-charge assumptions derived from binary synthetic salts.	Classical Nernst–Planck frameworks fail to predict dynamic pKa/pI speciation, localized proton flux, and severe co-ion competition inherent to live fermentates.	Formulate Coupled Reactive-Transport Models: Integrate Henderson–Hasselbalch acid–base equilibria and localized Poisson–Boltzmann electrostatics directly into multi-component Nernst–Planck transport algorithms.	Enables precision molecular fractionation of structural isomers and homologous biochemicals previously deemed thermodynamically inseparable.
2. Hierarchical Material Resilience	Electrochemical and Mechanical Degradation: Translating 2D laminates (MXenes, GO) and crystalline frameworks (MOFs, COFs) to industrial modules results in defect propagation and short operational lifetimes.	Reliance on ultra-thin free-standing films that are susceptible to interlayer swelling, binder dissolution, and Faradaic oxidation/Hofmann elimination during continuous voltage cycling.	Implement Accelerated Aging Protocols (AEP): Shift focus from pristine nanomaterials to robust, 3D-scaffolded, oxidation-resistant architectures capable of surviving radical attack and roll-to-roll (R2R) manufacturing.	Extends membrane lifetimes from days to years, lowering OpEx and de-risking the CapEx required for industrial deployment.
3. Thermodynamic Biofouling Defenses	Hydraulic Permeability vs. Interfacial Selectivity: Fouling is frequently evaluated strictly by measuring hydraulic flux decline, ignoring early-stage electrochemical passivation.	EPS and denatured proteins instantly mask fixed functional groups and alter interfacial dielectric constants, degrading permselectivity long before fluid permeability drops.	Engineer Active Self-Cleaning Interfaces: Integrate high-frequency asymmetric pulsed polarity reversal, localized micro-bubble generation, and define anti-fouling success strictly by the stabilization of SEC and permselectivity over extended operation.	Minimizes the need for chemical clean-in-place (CIP) protocols, ensuring stable, continuous operation in raw biological broths.

Table 7. Cont.

Strategic Research Domain	Identified Knowledge Gap and Scaling Bottleneck	Current Technological Limitation (Status Quo)	Actionable Engineering and Research Mandate	Target Industrial Impact (TRL 7–9)
4. Electro-Hydrodynamic Module Scaling	Macroscopic Fluid Maldistribution: Module scaling often assumes that permselectivity observed in small laboratory coupons ($\approx 10 \text{ cm}^2$) scales linearly to industrial stacks ($>100 \text{ m}^2$).	Unaddressed module-level physics: spacer shadowing, severe hydrodynamic channeling, localized Joule heating, and significant parasitic shunt currents through common distribution manifolds.	Re-Engineer Module Hydrodynamics: Utilize machine-learning-driven computational fluid dynamics (CFD) and 3D-printed fractal spacers to eliminate stagnant boundary layers, while redesigning manifolds to suppress shunt currents.	Guarantees that high permselectivity and current efficiency (η) observed in the laboratory are successfully replicated at the multi-megawatt commercial scale.
5. Cyber-Physical Integration and Control	Static Operation in Dynamic Environments: Industrial membrane stacks typically operate on static voltage or current set-points despite the fluctuating rheology and biological kinetics of live fermentations.	Lack of real-time interfacial sensing and reliance on slow manual interventions when concentration polarization, flux decline, or voltage spikes occur.	Deploy AI Digital Twins and In Situ EIS: Embed online multi-frequency Electrochemical Impedance Spectroscopy (EIS) to detect early scaling/fouling, enabling algorithms to autonomously modulate applied voltage in real time.	Transforms the membrane stack from a static downstream filter into an adaptive, self-optimizing platform capable of operating as a flexible load on renewable energy grids.
6. Total Flowsheet Consolidation (TEA/LCA)	Isolated Unit-Operation Evaluation: TEA and LCA frameworks frequently evaluate electro-membrane stacks as isolated components, ignoring upstream and downstream system boundaries.	Conventional extraction loops subject live microbial cultures to high-shear electric fields, causing cellular electroporation and trace nutrient depletion.	Evaluate via Flowsheet Consolidation: Decouple high-shear electric fields from live biomass using diffusion-limited or microfiltration pre-stages. Enforce TEA boundaries that quantify the elimination of downstream chemical tanks, evaporators, and secondary waste disposal.	Demonstrates that the economic superiority of electrified membranes stems from the simplification of the entire biorefinery flowsheet rather than isolated energy savings.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article as all information is based on previously published research, which has been cited accordingly.

Conflicts of Interest: The author declares no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ABE	Acetone–Butanol–Ethanol (Fermentation)
AEM	Anion Exchange Membrane
AEP	Accelerated Electrochemical Aging Protocol
AI	Artificial Intelligence
BMED/BPMED/EDBM	Bipolar Membrane Electrodialysis
BP/C	Bipolar/Cation Membrane Configuration
CapEx	Capital Expenditure
CDI	Capacitive Deionization
CED	Conventional Electrodialysis
CFD	Computational Fluid Dynamics
CIP	Clean-in-Place
CNT	Carbon Nanotube
COF	Covalent Organic Framework
DSA	Dimensionally Stable Anode
ED	Electrodialysis
EDI	Electrodeionization
EDL	Electrical Double Layer
EIS	Electrochemical Impedance Spectroscopy
EPS	Extracellular Polymeric Substances

EXS	Electrified Ion-Exchange Stripping
FCDI	Flow-Electrode Capacitive Deionization
GO	Graphene Oxide
IEC	Ion-Exchange Capacity
IEM	Ion-Exchange Membrane
ISPR	In Situ Product Recovery
LCA	Life Cycle Assessment
MCDI	Membrane Capacitive Deionization
MD	Molecular Dynamics
MXene	Transition Metal Carbides and Nitrides (e.g., $Ti_3C_2T_x$)
OpEx	Operating Expenditure
PEDOT	Poly(3,4-ethylenedioxythiophene)
PHA	Polyhydroxyalkanoate
PPy	Polypyrrole

References

- Pan, S.-Y.; Liao, Y.-L.; Lin, Y.-I.; Tseng, P.-C. Ionically Conductive Materials for Energy-Efficient Succinic Acid Recovery towards Electrified Circular Bioeconomy. *Bioresour. Technol.* **2025**, *430*, 132549. [[CrossRef](#)] [[PubMed](#)]
- Mesfun, S.; Gustafsson, G.; Larsson, A.; Samavati, M.; Furusjö, E. Electrification of Biorefinery Concepts for Improved Productivity—Yield, Economic and GHG Performances. *Energies* **2023**, *16*, 7436. [[CrossRef](#)]
- Beluhan, S.; Mihajlovski, K.; Šantek, B.; Ivančić Šantek, M. The Production of Bioethanol from Lignocellulosic Biomass: Pretreatment Methods, Fermentation, and Downstream Processing. *Energies* **2023**, *16*, 7003. [[CrossRef](#)]
- Janković, T.; Straathof, A.J.J.; Kiss, A.A. Process Systems Engineering Perspectives on Eco-Efficient Downstream Processing of Volatile Biochemicals from Fermentation. *Front. Energy Res.* **2024**, *11*, 1340612. [[CrossRef](#)]
- Liao, E.; Liu, N.; Li, Q.; Li, H.; Wang, L.; Wu, W. Dynamic Changes in Physicochemical Properties, Flavor, and Microbial Communities during Kombucha Fermentation with Dominant Autochthonous Strains Inoculation. *Food Res. Int.* **2025**, *222*, 117791. [[CrossRef](#)] [[PubMed](#)]
- Zhang, Z.; Guo, Y.; Quan, C.; Zhou, Y.; Song, Y.; Li, J.; Wang, D. Tuning Phosphorus Removal and Sludge Reduction Performance in S2EBPR Process by Regulating Sludge Retention Time in Side-Stream Anaerobic Reactor. *J. Water Process Eng.* **2025**, *70*, 107133. [[CrossRef](#)]
- Asghar, A.; Sairash, S.; Hussain, N.; Baqar, Z.; Sumrin, A.; Bilal, M. Current Challenges of Biomass Refinery and Prospects of Emerging Technologies for Sustainable Bioproducts and Bioeconomy. *Biofuels Bioprod. Biorefin.* **2022**, *16*, 1478–1494. [[CrossRef](#)]
- Castel, C.; Favre, E. Membrane Separations and Energy Efficiency. *J. Membr. Sci.* **2018**, *548*, 345–357. [[CrossRef](#)]
- Miladi, R.; Hadrich, B.; Frikha, N.; Gabsi, S. Comparative Analysis of Energy Recovery Configurations for Solar Vacuum Membrane Distillation. *Sustainability* **2025**, *17*, 8688. [[CrossRef](#)]
- Anim-Mensah, A.R. Pressure-Driven Polymeric Membrane Performance Prediction, New Membrane Dimensionless Number, and Considerations for Effective Membrane Design, Selection, Testing, and Operation. *Front. Membr. Sci. Technol.* **2025**, *3*, 1454589. [[CrossRef](#)]
- Oladipo, A.A.; Ahmad, M. Energy-Efficient Ion Recovery from Water Using Electro-Driven Membranes: A Comprehensive Critical Review. *Water* **2025**, *17*, 2456. [[CrossRef](#)]
- Handojo, L.; Wardani, A.K.; Regina, D.; Bella, C.; Kresnowati, M.T.A.P.; Wenten, I.G. Electro-Membrane Processes for Organic Acid Recovery. *RSC Adv.* **2019**, *9*, 7854–7869. [[CrossRef](#)] [[PubMed](#)]
- Zhang, L.; Hamelers, H.V.M.; Biesheuvel, P.M. Modeling Permeate PH in RO Membranes by the Extended Donnan Steric Partitioning Pore Model. *J. Membr. Sci.* **2020**, *613*, 118511. [[CrossRef](#)]
- Martí-Calatayud, M.C.; Ruiz-García, M.; Pérez-Herranz, V. On the Selective Transport of Mixtures of Organic and Inorganic Anions through Anion-Exchange Membranes: A Case Study about the Separation of Nitrates and Citric Acid by Electrodialysis. *Sep. Purif. Technol.* **2025**, *354*, 128951. [[CrossRef](#)]
- Bui, J.C.; Lees, E.W.; Liu, A.K.; Toh, W.L.; Stovall, T.N.; Goyal, P.; Galang, F.J.U.; Surendranath, Y.; Bell, A.T.; Weber, A.Z. Ion-Specific Phenomena Limit Energy Recovery in Forward-Biased Bipolar Membranes. *Nat. Chem. Eng.* **2024**, *2*, 63–76. [[CrossRef](#)]
- Chen, B.; Zhang, Z.; Jiang, C.; Fu, R.; Yan, J.; Wang, H.; Li, R.; Cao, G.; Wang, Y.; Xu, T. Electro-membrane Reactor: A Powerful Tool for Green Chemical Engineering. *AIChE J.* **2023**, *69*, e18140. [[CrossRef](#)]
- Zuo, K.; Garcia-Segura, S.; Cerrón-Calle, G.A.; Chen, F.-Y.; Tian, X.; Wang, X.; Huang, X.; Wang, H.; Alvarez, P.J.J.; Lou, J.; et al. Electrified Water Treatment: Fundamentals and Roles of Electrode Materials. *Nat. Rev. Mater.* **2023**, *8*, 472–490. [[CrossRef](#)]

18. Zhang, C.; Zhang, W.; Wang, Y. Diffusion Dialysis for Acid Recovery from Acidic Waste Solutions: Anion Exchange Membranes and Technology Integration. *Membranes* **2020**, *10*, 169. [[CrossRef](#)] [[PubMed](#)]
19. Xu, F.; Yuan, L.; Zhao, R.; Qin, B.; Zhang, F.; Ren, L.; Yang, H.; Yuan, M. Selective Ion Separation by Capacitive Deionization: A Comprehensive Review. *Materials* **2025**, *18*, 1107. [[CrossRef](#)] [[PubMed](#)]
20. Pan, X.; Li, Y.; Huang, Y.; Xu, J.; Sun, C.; Ye, Z.-L. Electrodialysis, a Promising Approach for Nutrients Recovery from Anaerobic Liquid Digestate: Status, Challenges and Perspectives. *J. Water Process Eng.* **2025**, *72*, 107658. [[CrossRef](#)]
21. Liu, W.; Livingston, J.L.; Wang, L.; Wang, Z.; del Cerro, M.; Younssi, S.A.; Epsztein, R.; Elimelech, M.; Lin, S. Pressure-Driven Membrane Desalination. *Nat. Rev. Methods Primers* **2024**, *4*, 10. [[CrossRef](#)]
22. Xia, S.; Liu, M.; Yu, H.; Zou, D. Pressure-Driven Membrane Filtration Technology for Terminal Control of Organic DBPs: A Review. *Sci. Total Environ.* **2023**, *904*, 166751. [[CrossRef](#)] [[PubMed](#)]
23. Haflich, H.M.; Singleton, J.W.; Coronell, O. Volatile Fatty Acid Selectivity during Electrodialysis: Effect of a Competing Counterion on Volatile Fatty Acid Transport Mechanisms. *J. Membr. Sci.* **2025**, *736*, 124703. [[CrossRef](#)] [[PubMed](#)]
24. Kim, K.-Y.; Shim, J.; Son, M.; Cho, K.H.; Jeon, B.-H. A Novel Electro-Sorption and Acidic Capturing Method for Continuous Volatile Fatty Acid Recovery. *Chem. Eng. J.* **2025**, *515*, 163822. [[CrossRef](#)]
25. Wu, J.; Ding, W.; Shen, N.; Song, H.; Li, Y.; Wang, G.; Chen, Y. Selective Separation of Volatile Fatty Acids and Phosphorous Recovery from Fermented Broth Using Flow-Electrode Capacitive Deionization. *Waste Manag.* **2023**, *165*, 12–18. [[CrossRef](#)]
26. Lee, M.; Kim, J.-H.; Yasin, M.; Moon, S.-H.; Chang, I.S. A Sustainable Bioprocessing System Leveraging Gas Fermentation and Bipolar Membrane Electrodialysis System for Direct Recovery of Acetic Acid. *Chem. Eng. J.* **2024**, *490*, 151710. [[CrossRef](#)]
27. Vecino, X.; Martínez-Arcos, A.; Cruz, J.M.; Moldes, A.B.; Cortina, J.L.; Reig, M. Exploring Electrodialysis Membrane Technology for the Purification of Biosurfactant Extracts and Recovery of Lactic Acid from Corn Steep Water. *Sep. Purif. Technol.* **2025**, *376*, 133889. [[CrossRef](#)]
28. Szczygielka, M.; Antczak, J.; Prochaska, K. Separation and Concentration of Succinic Acid from Post-Fermentation Broth by Bipolar Membrane Electrodialysis (EDBM). *Sep. Purif. Technol.* **2017**, *181*, 53–59. [[CrossRef](#)]
29. Im, S.; Jung, B.; Wang, X.; Wu, J.; Xiao, M.; Chen, X.; Quezada-Renteria, J.A.; Iddya, A.; Dlamini, D.; Lu, S.; et al. High-Efficiency Recovery of Acetic Acid from Water Using Electroactive Gas-Stripping Membranes. *Environ. Sci. Technol.* **2023**, *57*, 10096–10106. [[CrossRef](#)] [[PubMed](#)]
30. Herboth, R.; Gopakumar, G.; Coleman, C.; Wohler, M. Charge State Dependence of Amino Acid Propensity at Water Surface: Mechanisms Elucidated by Molecular Dynamics Simulations. *J. Phys. Chem. A* **2021**, *125*, 4705–4714. [[CrossRef](#)] [[PubMed](#)]
31. Tedesco, M.; Hamelers, H.V.M.; Biesheuvel, P.M. Nernst-Planck Transport Theory for (Reverse) Electrodialysis: I. Effect of Co-Ion Transport through the Membranes. *J. Membr. Sci.* **2016**, *510*, 370–381. [[CrossRef](#)]
32. Eliseeva, T.; Kharina, A. Desalination of Neutral Amino Acid Solutions in an Electromembrane System. *Membranes* **2022**, *12*, 665. [[CrossRef](#)] [[PubMed](#)]
33. Szczygielka, M.; Prochaska, K. Effective Separation of Bio-Based Alpha-Ketoglutaric Acid from Post-Fermentation Broth Using Bipolar Membrane Electrodialysis (EDBM) and Fouling Analysis. *Biochem. Eng. J.* **2021**, *166*, 107883. [[CrossRef](#)]
34. Liu, L.; Lan, H.; Cui, Y.; Tang, Q.; Bai, J.; An, X.; Sun, M.; Liu, H.; Qu, J. A Janus Membrane with Electro-Induced Multi-Affinity Interfaces for High-Efficiency Water Purification. *Sci. Adv.* **2024**, *10*, eadn8696. [[CrossRef](#)] [[PubMed](#)]
35. Luo, J.; Wan, Y. Mix-Charged Nanofiltration Membrane: Engineering Charge Spatial Distribution for Highly Selective Separation. *Chem. Eng. J.* **2023**, *464*, 142689. [[CrossRef](#)]
36. Liu, Y.; Tian, M.; Zhang, W.; Hu, B.; Deng, H. Enhancing Monovalent Selectivity of Cation Exchange Membranes by Electric Field-Assisted Interfacial Polymerization. *J. Membr. Sci.* **2025**, *733*, 124291. [[CrossRef](#)]
37. Sarkar, S.; SenGupta, A.K.; Prakash, P. The Donnan Membrane Principle: Opportunities for Sustainable Engineered Processes and Materials. *Environ. Sci. Technol.* **2010**, *44*, 1161–1166. [[CrossRef](#)] [[PubMed](#)]
38. Cairone, S.; Naddeo, V.; Belgiorio, V.; Taherzadeh, M.J.; Mahboubi, A. Evaluating the Impact of Membrane Properties and Feed PH on Concentration and Fractionation of Volatile Fatty Acid Using Nanofiltration. *J. Water Process Eng.* **2024**, *65*, 105793. [[CrossRef](#)]
39. Zhu, Y.; Gui, L.; Wang, R.; Wang, Y.; Fang, W.; Elimelech, M.; Lin, S.; Jin, J. Regulation of Molecular Transport in Polymer Membranes with Voltage-Controlled Pore Size at the Angstrom Scale. *Nat. Commun.* **2023**, *14*, 2373. [[CrossRef](#)] [[PubMed](#)]
40. Xing, J.; Zhang, H.; Wei, G.; Hong, T.; Chen, S.; Liang, H.; Quan, X. Electro-Responsive OCNT/PPy Membrane for Efficient Irreversible-Fouling Control through Electroreregulation of Electrostatic and Fluid Interaction Forces. *Chem. Eng. J.* **2024**, *494*, 153218. [[CrossRef](#)]
41. Sun, M.; Wang, X.; Winter, L.R.; Zhao, Y.; Ma, W.; Hedtke, T.; Kim, J.-H.; Elimelech, M. Electrified Membranes for Water Treatment Applications. *ACS ES T Eng.* **2021**, *1*, 725–752. [[CrossRef](#)]
42. Long, Z.; Meng, J.; Weddle, L.R.; Videla, P.E.; Menzel, J.P.; Cabral, D.G.A.; Liu, J.; Qiu, T.; Palasz, J.M.; Bhattacharyya, D.; et al. The Impact of Electric Fields on Processes at Electrode Interfaces. *Chem. Rev.* **2025**, *125*, 1604–1628. [[CrossRef](#)] [[PubMed](#)]

43. Kim, N.; Elbert, J.; Kim, C.; Su, X. Redox-Copolymers for Nanofiltration-Enabled Electrodialysis. *ACS Energy Lett.* **2023**, *8*, 2097–2105. [[CrossRef](#)]
44. Kim, G.; Kim, H.; Kim, M.; Kim, D.; Kim, Y.; Kim, S.; Kim, C. Effect of Redox Couples on Desalination Performance in Redox-Mediated Electrodialysis. *Sep. Purif. Technol.* **2026**, *390*, 137002. [[CrossRef](#)]
45. Dischinger, S.M.; Miller, D.J.; Vermaas, D.A.; Kingsbury, R.S. Unifying the Conversation: Membrane Separation Performance in Energy, Water, and Industrial Applications. *ACS ES T Eng.* **2024**, *4*, 277–289. [[CrossRef](#)] [[PubMed](#)]
46. Wang, L.; Patel, S.K.; Elimelech, M. Correlation Equation for Evaluating Energy Consumption and Process Performance of Brackish Water Desalination by Electrodialysis. *Desalination* **2021**, *510*, 115089. [[CrossRef](#)]
47. Doyen, A.; Roblet, C.; Beaulieu, L.; Saucier, L.; Pouliot, Y.; Bazinet, L. Impact of Water Splitting Phenomenon during Electrodialysis with Ultrafiltration Membranes on Peptide Selectivity and Migration. *J. Membr. Sci.* **2013**, *428*, 349–356. [[CrossRef](#)]
48. Vasil'eva, V.I.; Akberova, E.M.; Saud, A.M.; Zabolotsky, V.I. Current-Voltage Characteristics of Membranes with Different Cation-Exchanger Content in Mineral Salt—Neutral Amino Acid Solutions under Electrodialysis. *Membranes* **2022**, *12*, 1092. [[CrossRef](#)] [[PubMed](#)]
49. Liu, H.; Li, J.; Zhao, S.; Yue, F.; Sun, Y.; Zhu, M.; Wang, S.; Zhang, Y.; Feng, X.; Wang, B. Metal–Organic Frameworks with Enhanced Electret Capability for Selective Electrostatic Separation. *J. Am. Chem. Soc.* **2025**, *147*, 40331–40337. [[CrossRef](#)] [[PubMed](#)]
50. Guo, S.; Zhang, H.; Chen, X.; Feng, S.; Wan, Y.; Luo, J. Fabrication of Antiswelling Loose Nanofiltration Membranes via a “Selective-Etching-Induced Reinforcing” Strategy for Bioseparation. *ACS Appl. Mater. Interfaces* **2021**, *13*, 19312–19323. [[CrossRef](#)] [[PubMed](#)]
51. Qi, S.; Zhang, W.; Ramon, G.Z.; Ronen, A. Sustainable Ammonia Recovery in Electrochemical Membranes: The Critical Role of Electromigration. *J. Membr. Sci.* **2025**, *726*, 124018. [[CrossRef](#)]
52. Wang, X.; Im, S.; Jung, B.; Wu, J.; Iddya, A.; Javier, Q.-R.A.; Xiao, M.; Ma, S.; Lu, S.; Jaewon, B.; et al. Simple and Low-Cost Electroactive Membranes for Ammonia Recovery. *Environ. Sci. Technol.* **2023**, *57*, 9405–9415. [[CrossRef](#)] [[PubMed](#)]
53. Poitras, D.; Perreault, V.; Gaaloul, S.; Schuck, P.; Bazinet, L. Lactic Acid Removal and Demineralization of Acid Whey by Coupling Electrodialysis under Pulsed Electric Fields with Pre-Concentration by Nanofiltration: Impact on Spray Drying and Powder Quality. *Desalination* **2025**, *613*, 119032. [[CrossRef](#)]
54. Gausmann, M.; Gössi, A.; Bertram, F.; Riedl, W.; Schuur, B.; Jupke, A. Electrochemical Membrane-Assisted PH-Swing Extraction and Back-Extraction of Lactic Acid. *Sep. Purif. Technol.* **2022**, *289*, 120702. [[CrossRef](#)]
55. Richa, M.; García-Cervilla, R.; Lobato, J.; Cañizares, P.; Rodrigo, M.A. Separation of Carboxylates Using Electrodialysis: A Key Process for the Electro-Refinery Concept. *Sep. Purif. Technol.* **2025**, *376*, 134073. [[CrossRef](#)]
56. Richa, M.; García-Cervilla, R.; Lobato, J.; Cañizares, P.; Rodrigo, M.A. Carboxylic Acids Selective Recovery from Wastewater Using Electrodialysis. *J. Environ. Chem. Eng.* **2025**, *13*, 117752. [[CrossRef](#)]
57. Lu, S.; McGaughey, A.; Im, S.; Liu, Y.; Wang, X.; Leininger, A.; Jassby, D.; Hoek, E.; Ren, Z.J. Membrane Electrolysis Distillation for Volatile Fatty Acids Extraction from PH-Neutral Fermented Wastewater. *Water Res.* **2024**, *265*, 122306. [[CrossRef](#)] [[PubMed](#)]
58. Barros, K.S.; Marreiros, B.C.; Martí-Calatayud, M.C.; Crespo, J.G.; Pérez-Herranz, V.; Velizarov, S. Effect of PH on the Selective Electrodialytic Recovery of Acidogenic-Derived Volatile Fatty Acids. *Sep. Purif. Technol.* **2025**, *364*, 132550. [[CrossRef](#)]
59. Barros, K.S.; Carvalho, M.; Marreiros, B.C.; Reis, M.A.M.; Crespo, J.G.; Pérez-Herranz, V.; Velizarov, S. Donnan Dialysis for Recovering Ammonium from Fermentation Solutions Rich in Volatile Fatty Acids. *Membranes* **2023**, *13*, 347. [[CrossRef](#)] [[PubMed](#)]
60. Bui, J.C.; Lees, E.W.; Marin, D.H.; Stovall, T.N.; Chen, L.; Kusoglu, A.; Nielander, A.C.; Jaramillo, T.F.; Boettcher, S.W.; Bell, A.T.; et al. Multi-Scale Physics of Bipolar Membranes in Electrochemical Processes. *Nat. Chem. Eng.* **2024**, *1*, 45–60. [[CrossRef](#)]
61. Gu, M.; Li, M.; Gao, Y.; Ding, H.; Liang, S.; Huang, X. Pivotal Influence of Solution Chemistry on Electrosorption-Enhanced Membrane Filtration Performance: Implication for Study of Electrified Membrane Processes. *Water Res.* **2025**, *279*, 123434. [[CrossRef](#)] [[PubMed](#)]
62. Lucas, É.; Bui, J.C.; Stovall, T.N.; Hwang, M.; Wang, K.; Dunn, E.R.; Spickermann, E.; Shiau, L.; Kusoglu, A.; Weber, A.Z.; et al. Asymmetric Bipolar Membrane for High Current Density Electrodialysis Operation with Exceptional Stability. *ACS Energy Lett.* **2024**, *9*, 5596–5605. [[CrossRef](#)]
63. Dash, S.R.; Bose, P.; Alam, M.K.; Kim, J. Anaerobic Electrochemical Membrane Bioreactors: A Panoramic Tool for Wastewater Treatment and Resource Recovery. *Crit. Rev. Environ. Sci. Technol.* **2025**, *55*, 465–482. [[CrossRef](#)]
64. Xie, H.; Qu, C.; Wang, X.; Li, H.; Liu, Z.; Qin, Z.; Liang, Q.; Liu, Y.; Zhang, Y. Process Intensification of Phenol Recovery via Carrier-Conducted Membrane Electrodialysis with Improved Transport and Selectivity Control. *J. Hazard. Mater.* **2026**, *503*, 141096. [[CrossRef](#)] [[PubMed](#)]
65. Kim, N.; Lee, J.; Su, X. Precision Tuning of Highly Selective Polyelectrolyte Membranes for Redox-Mediated Electrochemical Separation of Organic Acids. *Adv. Funct. Mater.* **2023**, *33*, 2211645. [[CrossRef](#)]
66. Kekre, K.M.; Anvari, A.; Kahn, K.; Yao, Y.; Ronen, A. Reactive Electrically Conducting Membranes for Phosphorus Recovery from Livestock Wastewater Effluents. *J. Environ. Manag.* **2021**, *282*, 111432. [[CrossRef](#)] [[PubMed](#)]

67. Kim, N.; Aguda, A.; Kim, C.; Su, X. Redox-Mediated Electrodialysis for Desalination, Environmental Remediation, and Resource Recovery. *ACS Energy Lett.* **2024**, *9*, 3887–3912. [\[CrossRef\]](#)
68. Kim, N.; Jeon, J.; Elbert, J.; Kim, C.; Su, X. Redox-Mediated Electrochemical Desalination for Waste Valorization in Dairy Production. *Chem. Eng. J.* **2022**, *428*, 131082. [\[CrossRef\]](#)
69. He, X.; Huang, Y.; An, M.; Fu, J.; Wu, D.; Qi, S.; Yi, C. Electric-Field-Assisted Arrangement of Carbon Nanotube inside PDMS Membrane Matrix for Efficient Bio-Ethanol Recovery via Pervaporation. *Sep. Purif. Technol.* **2024**, *334*, 125952. [\[CrossRef\]](#)
70. Jin, L.; Ren, Y.; Zheng, W.; Pan, F.; You, S.; Liu, Y. Surface Engineering of Electrified MXene Filter for Enhanced Phosphate Removal. *ACS ES T Eng.* **2023**, *3*, 2243–2251. [\[CrossRef\]](#)
71. Zhang, W.; Wang, Z.; Wang, P.; Wang, Z.; Cheng, W.; Ma, J. Efficient Cation Sieving and Recovery via Synergistic Nanoconfinement and Ionic Anchoring in Engineered PSS-Functionalized Nanochannel Membranes. *Water Res.* **2026**, *294*, 125529. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Luo, Y.; Liu, Y.; Shen, J.; Van der Bruggen, B. Application of bipolar membrane electrodialysis in environmental protection and resource recovery: A review. *Membranes* **2022**, *12*, 829. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Deemer, E.M.; Xu, P.; Verduzco, R.; Shane Walker, W. Challenges and Opportunities for Electro-Driven Desalination Processes in Sustainable Applications. *Curr. Opin. Chem. Eng.* **2023**, *42*, 100972. [\[CrossRef\]](#)
74. Liang, C.-M.; Wang, C.-C.; Hung, Y.-T.; Cheng, H.-W.; Yang, C.-F. Optimization of Operating Parameters for 2,5-Furandicarboxylic Acid Recovery Using Electrodialysis with Bipolar Membrane and Traditional Electrodialysis Systems. *Heliyon* **2024**, *10*, e34706. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Barros, K.S.; Marreiros, B.C.; Reis, M.A.M.; Crespo, J.G.; Pérez-Herranz, V.; Velizarov, S. Recovery and Fractionation of Volatile Fatty Acids from Fermented Solutions by Electrodialysis: Electrochemical Characterization of Anion-Exchange Membranes. *J. Environ. Chem. Eng.* **2024**, *12*, 114457. [\[CrossRef\]](#)
76. Mandal, P.; Mondal, R.; Goel, P.; E., B.; Chatterjee, U.; Chattopadhyay, S. Selective Recovery of Carboxylic Acid through PVDF Blended Anion Exchange Membranes Using Electrodialysis. *Sep. Purif. Technol.* **2022**, *292*, 121069. [\[CrossRef\]](#)
77. Ge, X.; Li, B.; Meng, X.; He, T.; Li, T.; Yang, Q.; Wei, Z.; Yan, T.; Yuan, Z. Study on the Separation of Nitric Acid and Acetic Acid Using Multi-Stage Electrodialysis. *Desalination* **2025**, *608*, 118838. [\[CrossRef\]](#)
78. Huang, Y.; Wang, Y.; Shang, N.; Li, P. Microbial Fermentation Processes of Lactic Acid: Challenges, Solutions, and Future Prospects. *Foods* **2023**, *12*, 2311. [\[CrossRef\]](#) [\[PubMed\]](#)
79. Mancini, E.; Ramin, P.; Styrbæck, P.; Bjergholt, C.; Soheil Mansouri, S.; Gernaey, K.V.; Luo, J.; Pinelo, M. Separation of Succinic Acid from Fermentation Broth: Dielectric Exclusion, Donnan Effect and Diffusion as the Most Influential Mass Transfer Mechanisms. *Sep. Purif. Technol.* **2022**, *281*, 119904. [\[CrossRef\]](#)
80. Jiménez-Páez, E.; Ortiz, J.M.; Vega-de Armas, A.J.; Feroso, F.G.; Serrano, A. Recovery of Volatile Fatty Acids from an Olive Mill Solid Waste Ferment via Electrodialysis: A Comparative Study with Synthetic Mixtures. *ACS Sustain. Chem. Eng.* **2026**, *14*, 10432–10440. [\[CrossRef\]](#)
81. Melnikov, S.S.; Nosova, E.N.; Melnikova, E.D.; Zabolotsky, V.I. Reactive separation of inorganic and organic ions in electrodialysis with bilayer membranes. *Sep. Purif. Technol.* **2021**, *268*, 118561. [\[CrossRef\]](#)
82. Papadopoulou, E.; González, M.C.; Reif, D.; Ahmed, A.; Tsapekos, P.; Angelidaki, I.; Harasek, M. Separation of Lactic Acid from Fermented Residual Resources Using Membrane Technology. *J. Environ. Chem. Eng.* **2023**, *11*, 110881. [\[CrossRef\]](#)
83. Xu, S.; Zhang, L.; Zhang, Z.; Xie, L.; Zhang, W. The Enrichment of Acetic Acid Using an Integrated Reverse Osmosis–Electrodialysis Process. *Membranes* **2025**, *15*, 129. [\[CrossRef\]](#) [\[PubMed\]](#)
84. Kotoka, F.; Gutierrez, L.; Verliefde, A.; Cornelissen, E. Selective Separation of Nutrients and Volatile Fatty Acids from Food Wastes Using Electrodialysis and Membrane Contactor for Resource Valorization. *J. Environ. Manag.* **2024**, *354*, 120290. [\[CrossRef\]](#) [\[PubMed\]](#)
85. Malanca, A.A.; Mancini, E.; Yusuf, M.; Khensir, G.K.; Mansouri, S.S.; Skiadas, I.V.; Gavala, H.N.; Pinelo, M. Variables and Mechanisms Affecting Electro-Membrane Extraction of Bio-Succinic Acid from Fermentation Broth. *Membranes* **2022**, *12*, 542. [\[CrossRef\]](#) [\[PubMed\]](#)
86. Fufa, M.; Song, X.; Gul, S.; Liang, W.; Yan, B.; Zhang, Y.; Jiang, H. Maximizing Volatile Fatty Acid Yields from Sewage Sludge: Electrodialysis with Bipolar Membranes Enhanced Fermentation Driven by Heat-Alkali Pretreatment and PH Optimization. *Bioresour. Technol.* **2025**, *438*, 133151. [\[CrossRef\]](#) [\[PubMed\]](#)
87. Wang, H.; Yan, J.; Fu, R.; Yan, H.; Jiang, C.; Wang, Y.; Xu, T. Bipolar Membrane Electrodialysis for Cleaner Production of Gluconic Acid: Valorization of the Regenerated Base for the Upstream Enzyme Catalysis. *Ind. Eng. Chem. Res.* **2022**, *61*, 7634–7644. [\[CrossRef\]](#)
88. van der Wal, M.; Rovai, R.; Nijmeijer, K.; Borneman, Z. Bipolar Membrane Electrodialysis Enhanced Nutrient Separation in Manure Treatment. *Environ. Technol. Innov.* **2025**, *39*, 104326. [\[CrossRef\]](#)
89. Sun, Y.; Wang, Y.; Peng, Z.; Liu, Y. Treatment of High Salinity Sulfanilic Acid Wastewater by Bipolar Membrane Electrodialysis. *Sep. Purif. Technol.* **2022**, *281*, 119842. [\[CrossRef\]](#)

90. Kulkarni, T.; Al Dhamen, A.M.I.; Bhattacharya, D.; Arges, C.G. Bipolar Membrane Capacitive Deionization for PH-Assisted Ionic Separations. *ACS ES T Eng.* **2023**, *3*, 2171–2182. [[CrossRef](#)]
91. Kaniadakis, I.; van Lier, J.B.; Spanjers, H. Ammonia Recovery in Bipolar Membrane Electrodialysis via PH Control through Electric Current Pulse Modulation. *Water Res.* **2025**, *286*, 124185. [[CrossRef](#)] [[PubMed](#)]
92. Lugo, A.; Ahmed, M.F.; Oddonetto, T.L.; Senanayake, P.S.; Basnayake, I.; Stoll, Z.; Ehsani, M.; Moe, N.E.; Barber, J.; Wang, H.; et al. Operational Optimization of Bipolar Membrane Electrodialysis for Acid and Base Production in Zero Liquid Discharge of High-Salinity Brine. *Desalination* **2025**, *615*, 119290. [[CrossRef](#)]
93. León, T.; Abdullah Shah, S.; López, J.; Culcasi, A.; Jofre, L.; Cipollina, A.; Cortina, J.L.; Tamburini, A.; Micale, G. Electrodialysis with Bipolar Membranes for the Generation of NaOH and HCl Solutions from Brines: An Inter-Laboratory Evaluation of Thin and Ultrathin Non-Woven Cloth-Based Ion-Exchange Membranes. *Membranes* **2022**, *12*, 1204. [[CrossRef](#)] [[PubMed](#)]
94. Herrero-Gonzalez, M.; López, J.; Virruso, G.; Cassaro, C.; Tamburini, A.; Cipollina, A.; Cortina, J.L.; Ibañez, R.; Micale, G. Analysis of Operational Parameters in Acid and Base Production Using an Electrodialysis with Bipolar Membranes Pilot Plant. *Membranes* **2023**, *13*, 200. [[CrossRef](#)] [[PubMed](#)]
95. Wang, L.; Dong, Z.; Liu, P.; Qu, C.; Zhang, R.; Wang, X.; Tan, M.; Cong, W.; Liu, Y.; Zhang, Y. Boosting Acid/Base Production in Bipolar Membrane Electrodialysis via Proton Blocking Polymer Inclusion Membranes. *J. Membr. Sci.* **2025**, *735*, 124543. [[CrossRef](#)]
96. Hussain, A.; Yan, H.; Ul Afsar, N.; Jiang, C.; Wang, Y.; Xu, T. Multistage-Batch Bipolar Membrane Electrodialysis for Base Production from High-Salinity Wastewater. *Front. Chem. Sci. Eng.* **2022**, *16*, 764–773. [[CrossRef](#)]
97. Lü, X.; Shao, S.; Wu, J.; Zhao, Y.; Lu, B.; Li, J.; Liang, L.; Tian, L. Recovery of Acid and Alkaline from Industrial Saline Wastewater by Bipolar Membrane Electrodialysis under High-Chemical Oxygen Demand Concentration. *Molecules* **2022**, *27*, 7308. [[CrossRef](#)] [[PubMed](#)]
98. Kim, H.; Kim, S.; Lee, B.; Kim, M.; Kim, G.; Kim, C. Valorization of Na₂SO₄ in Wastewater from Spent Lithium-Ion Battery Recycling Using Redox-Mediated Bipolar Membrane Electrodialysis. *Chem. Eng. J.* **2025**, *504*, 158834. [[CrossRef](#)]
99. Cassaro, C.; Virruso, G.; Cipollina, A.; Fagiolini, A.; Tamburini, A.; Micale, G. Enhanced Schemes for Brine Valorization via Electrodialysis with Bipolar Membranes Powered by Renewable Energy. *ACS Omega* **2025**, *10*, 10122–10138. [[CrossRef](#)] [[PubMed](#)]
100. Valentino, L.; Alejandre, A. Capacitive Deionization for the Extraction and Recovery of Butyrate. *ACS Sustain. Chem. Eng.* **2023**, *11*, 6385–6394. [[CrossRef](#)]
101. Wagner, R.; Winger, S.; Franzreb, M. Predicting the Potential of Capacitive Deionization for the Separation of PH-dependent Organic Molecules. *Eng. Life Sci.* **2021**, *21*, 589–606. [[CrossRef](#)] [[PubMed](#)]
102. Wang, C.; Li, R.; Xu, Y.; Ma, Z.; Qiu, Y.; Wang, C.; Ren, L.-F.; Shao, J. Effective Electrosorption and Recovery of Phosphorus by Capacitive Deionization with a Covalent Organic Framework-Membrane Coating Electrode. *Desalination* **2024**, *570*, 117088. [[CrossRef](#)]
103. Qu, Y.; Lu, Y.; Li, J.; Ko, J.; Xu, Q. Goethite-Modified Peanut Shell Biochar for Selective Phosphate Recovery from Digestate-Derived Permeate via Membrane Capacitive Deionization. *Green Energy Resour.* **2026**, *4*, 100183. [[CrossRef](#)]
104. Qu, Y.; Li, J.; Lu, Y.; Huang, D.; Ko, J.; Xu, Q. Selective Phosphate Separation and Enrichment from Real Digestate via Membrane Capacitive Deionization Using LDH/Biochar Composite Electrodes. *Sep. Purif. Technol.* **2026**, *391*, 137094. [[CrossRef](#)]
105. Yang, F.; Chen, S.; Liang, S.; Wen, M.; Quan, J.; Shi, X.; Yuan, S.; Duan, H.; Yu, W.; Huang, L.; et al. Efficient Phosphorus Recovery from Simulated Phosphoric Acid Wastewater Using a Tailored Dual-Module Flow Electrode Capacitive Deionization (FCDI) Strategy. *Resour. Conserv. Recycl.* **2024**, *211*, 107867. [[CrossRef](#)]
106. Jiang, J.; Dorji, P.; Badeti, U.; Sohn, W.; Freguia, S.; Phuntsho, S.; El Saliby, I.; Shon, H.K. Potential Nutrient Recovery from Source-Separated Urine through Hybrid Membrane Bioreactor and Membrane Capacitive Deionisation. *Desalination* **2023**, *566*, 116924. [[CrossRef](#)]
107. Sidik, F.; Lin, J.-L.; Juang, Y.-J.; Lin, G.-Y. Energy-Efficient Recovery of Ammonium by Flow-Electrode Capacitive Deionization Using Graphene-Activated Carbons. *Sep. Purif. Technol.* **2026**, *386*, 136477. [[CrossRef](#)]
108. Mansoor, N.E.; Diaz, L.A.; Shuck, C.E.; Gogotsi, Y.; Lister, T.E.; Estrada, D. Removal and Recovery of Ammonia from Simulated Wastewater Using Ti₃C₂T_x MXene in Flow Electrode Capacitive Deionization. *npj Clean Water* **2022**, *5*, 26. [[CrossRef](#)]
109. Wu, G.-Y.; Pu, Y.; Wang, Y.; Zhang, H.; Wu, Q.; Zeng, R.J.; Jiang, Y. Selective Recovery of Medium-Chain Fatty Acids from Secondary Fermentation Broth by Flow-Electrode Capacitive Deionization. *Chem. Eng. J.* **2023**, *470*, 144168. [[CrossRef](#)]
110. Song, J.; Zhao, X.; Liu, R.; Wang, Y.; Zhu, D.; Wang, X.; Jiang, K.; Wu, D. Simultaneous Removal and Recovery of Ammonium and Phosphate Ions Using Flow Electrode Capacitive Deionization through the Struvite Generation Mechanism. *Sep. Purif. Technol.* **2025**, *358*, 130395. [[CrossRef](#)]
111. Zeng, R.; Yang, L.-H.; Zhai, S.-Y.; Liu, C.-Y.; Lin, N.; Ou-Yang, Q.-H.; Xu, Y.-H.; Wang, A.-J.; Cheng, H.-Y. Phenol-Driven Ammonium Recovery from Coal Chemical Wastewater in a Bioelectrochemical System (BES). *J. Hazard. Mater.* **2025**, *490*, 137791. [[CrossRef](#)] [[PubMed](#)]
112. Boto, S.T.; Cristiani, L.; Rosenbaum, M.A. Biochemical Production with Microbial Bioelectrochemical Systems. *Curr. Opin. Biotechnol.* **2025**, *93*, 103291. [[CrossRef](#)] [[PubMed](#)]

113. Wang, J.; Chen, M.; Zhang, J.; Sun, X.; Li, N.; Wang, X. Dynamic Membrane Filtration Accelerates Electroactive Biofilms in Bioelectrochemical Systems. *Environ. Sci. Ecotechnol.* **2024**, *20*, 100375. [[CrossRef](#)] [[PubMed](#)]
114. Burns, M.; Tang, H.; Larson, R.A.; Qin, M. Bioelectrochemically-Assisted Ammonia Recovery from Dairy Manure. *Water Res.* **2024**, *252*, 121243. [[CrossRef](#)] [[PubMed](#)]
115. Cheng, K.Y.; Kaksonen, A.H.; Cord-Ruwisch, R. Bioelectrochemical Extraction of Ammonium from Low-Strength Wastewater with Concomitant Generation of High-Purity Hydrogen. *Environ. Technol.* **2026**, *47*, 1007–1018. [[CrossRef](#)] [[PubMed](#)]
116. Ul, Z.; Galeano, M.B.; Sulonen, M.; Baeza, M.; Baeza, J.A.; Guisasola, A. Electrochemical and Bioelectrochemical Ammonium Recovery from N-Loaded Streams Using a Hydrophobic Membrane. *Bioelectrochemistry* **2025**, *166*, 109013. [[CrossRef](#)] [[PubMed](#)]
117. Ul, Z.; Sulonen, M.; Baeza, J.A.; Guisasola, A. Continuous High-Purity Bioelectrochemical Nitrogen Recovery from High N-Loaded Wastewaters. *Bioelectrochemistry* **2024**, *158*, 108707. [[CrossRef](#)] [[PubMed](#)]
118. Mohamed, A.A.R.; Ali, A.E.-D.; Hassouna, M.S.E.-D.; Elhusseiny, A.F.; He, Z.; Moustafa, H. Efficacy of Bioelectrochemical and Electrochemical Systems in Ammonia Recovery from Slaughterhouse Wastewater. *Appl. Water Sci.* **2025**, *15*, 28. [[CrossRef](#)]
119. Chang, C.-C.; Wu, C.-Y.; Jiang, J.-Z.; Hsu, C.-A.; Yu, C.-P.; Lin, Y.-L. Development of an Alkali-Producing Bioelectrochemical System for Sewage-Polluted Seawater: Nutrient Removal, Scalant Mitigation, and Resource Recovery. *J. Water Process Eng.* **2025**, *74*, 107834. [[CrossRef](#)]
120. Zhang, Y.; Wang, Y.; Chen, Z.; Hu, C.; Qu, J. Recovering Nutrients and Unblocking the Cake Layer of an Electrochemical Anaerobic Membrane Bioreactor. *Nat. Commun.* **2024**, *15*, 9111. [[CrossRef](#)] [[PubMed](#)]
121. Wen, P.; Dai, S.; Ge, Z. Phosphorus Resource Recovery Based on a Bio-Electrodialysis System. *Environ. Sci.* **2026**, *12*, 908–919. [[CrossRef](#)]
122. Saabas, D.; Lee, J. Recovery of Ammonia from Simulated Membrane Contactor Effluent Using Bipolar Membrane Electrodialysis. *J. Membr. Sci.* **2022**, *644*, 120081. [[CrossRef](#)]
123. Çelik, A.; Aksoy, Y.; Hanay, Ö.; Yegin, M.; Köse, Y.; Demirelli, K.; Hasar, H. Fabrication and characterization of Ti₃C₂T_x MXene-based bipolar membrane. *J. Appl. Electrochem.* **2025**, *55*, 1281–1294. [[CrossRef](#)]
124. Nour, A.; Iqbal, W.; Navarro-Alapont, J.; Ferrando-Soria, J.; Magarò, P.; Elliani, R.; Tagarelli, A.; Maletta, C.; Mastropietro, T.F.; Pardo, E.; et al. Efficient Nickel and Cobalt Recovery by Metal–Organic Framework-Based Mixed Matrix Membranes (MMM-MOFs). *ACS Sustain. Chem. Eng.* **2024**, *12*, 12014–12028. [[CrossRef](#)] [[PubMed](#)]
125. Fang, D.; Song, X.; Li, C.; Li, F.; Zhang, P.; Lv, C.; Li, K. Faradic Side Reactions at Ti₃C₂T_x-Based Cathode for Ammonium Extraction Studied in a Novel PG-MCDI System. *Chem. Eng. J.* **2024**, *485*, 149334. [[CrossRef](#)]
126. Strathmann, H.; Grabowski, A.; Eigenberger, G. Ion-Exchange Membranes in the Chemical Process Industry. *Ind. Eng. Chem. Res.* **2013**, *52*, 10364–10379. [[CrossRef](#)]
127. Yang, X.; Wei, G.; Cao, J.; Ding, Z.; Yuan, R.; Long, J.; Xu, C. Mxene-Cu Electrified Membranes with Confined Lamellar Channels for the Flow-through Electrochemical Reduction of Nitrate to Ammonia. *ACS Sustain. Chem. Eng.* **2024**, *12*, 3378–3389. [[CrossRef](#)]
128. Choudhury, A.; Patnaik, P.; Mondal, R.; Sarkar, S.; Chatterjee, U. GO-Anchored Imidazolium Based Cross-Linked Composite Anion Exchange Membranes for the Enhancement in Acid Recovery via Diffusion Dialysis. *Chem. Eng. J.* **2023**, *451*, 138901. [[CrossRef](#)]
129. Mehdiinia Lichaei, M.; Pazani, F.; Aroujalian, A.; Rodrigue, D. Two-Step Surface Functionalization/Alignment Strategy to Improve CO₂/N₂ Separation from Mixed Matrix Membranes Based on PEBAX and Graphene Oxide. *Process Saf. Environ. Prot.* **2022**, *163*, 36–47. [[CrossRef](#)]
130. Wang, S.; Huang, Y.; Qiang, Y.; Wu, M.; Liang, S.; Wang, J.; Fang, C.; Zhu, L. Nanoconfined Electrostatic Interaction for Efficient Anion Sieving in Graphene Oxide Membranes. *Water Res.* **2025**, *270*, 122855. [[CrossRef](#)] [[PubMed](#)]
131. Li, J.; Xu, C.; Long, J.; Ding, Z.; Yuan, R.; Li, Z. Lamellar MXene Nanofiltration Membranes for Electrostatic Modulation of Molecular Permeation: Implications for Fine Separation. *ACS Appl. Nano Mater.* **2022**, *5*, 7373–7381. [[CrossRef](#)]
132. Fang, X.; Shi, M.; Zhang, Z.; Zhang, X.; Yan, X.; Li, F.; Jiang, S.; Liu, Y. Electric Field-Assisted Ultra-Thin MXene Conductive Nanofiltration Membrane for Efficient Dye/Salt Separation. *Sep. Purif. Technol.* **2024**, *339*, 126753. [[CrossRef](#)]
133. Fang, D.; Liu, F.; Li, F.; Zhang, P.; Li, C.; Qiu, X.; Lv, C.; Zhang, X.; Li, K. Electrochemical Membrane Systems for Remediating Ammonium-Containing Wastewater via Coupling Capacitance Adsorption and Oxygen Reduction. *Chem. Eng. J.* **2024**, *498*, 155218. [[CrossRef](#)]
134. Xie, D.; Wang, Q.; Liang, D. Selective ammonium separation by capacitive deionization using binder-free MXene/PBA-coated activated carbon electrodes. *Desalination* **2026**, *637*, 120470. [[CrossRef](#)]
135. Li, W.; Jin, L.; Jiang, S.; Liu, Y. Electrified Nitrogen-Doped MXene Membrane Electrode for Micropollutants Decontamination via Peroxymonosulfate Activation. *ACS ES T Eng.* **2024**, *4*, 176–185. [[CrossRef](#)]
136. Jiang, Y.; Fu, W.; Ding, Z.; Yuan, R.; Long, J.; Xu, C. Efficient Electrochemical Hydrogenation of Biomass within Consecutive Nanoconfined Channels of MXene-Based Electrified Membrane Electrodes. *ACS Sustain. Chem. Eng.* **2026**, *14*, 11138–11150. [[CrossRef](#)]

137. Halisdemir, U.; Çelik, A.; Yegin, M.; Köse, Y.; Hanay, Ö. Design and Application of Ti4N3Tx-Functionalized Bipolar Membranes for Sustainable Acid and Base Production via BMED System. *J. Appl. Electrochem.* **2026**, *56*, 80. [\[CrossRef\]](#)
138. Qiu, Y.; Gao, Y.; Liu, J.R.; Cai, Y.; Mei, Y.; Xia, L.; Ng, H.Y.; Zhao, Y.; Van der Bruggen, B.; Tang, C. In-Situ Construction of ZIF-Embedded Hydrogel Electro-Driven Membranes for Lithium Selectivity. *J. Membr. Sci.* **2026**, *741*, 125043. [\[CrossRef\]](#)
139. Yu, H.; Hossain, S.M.; Wang, C.; Choo, Y.; Naidu, G.; Han, D.S.; Shon, H.K. Selective Lithium Extraction from Diluted Binary Solutions Using Metal-Organic Frameworks (MOF)-Based Membrane Capacitive Deionization (MCDI). *Desalination* **2023**, *556*, 116569. [\[CrossRef\]](#)
140. Baig, N.; Abdulazeez, I.; Salhi, B.; Asmaly, H.A.; Osman, A.I.; Ahmed, K.H. Electro-Assisted Interfacial Growth of Biomimetic KFUPM-100 MOF Membrane for Ultrafast Oil-Water Separation with Breakthrough Stability. *Chem. Eng. J.* **2025**, *504*, 158628. [\[CrossRef\]](#)
141. Yang, H.; Zhang, W.; Zhang, H.; Tan, Q.; Zhang, X.; Yang, X.; Meng, F.; Zhao, S. Electric Field Responsive Carbon Nanotube-Based Polyamide Membrane for Enhanced Antibiotics Separation: From Charge Regulation to Performance Enhancement. *J. Membr. Sci.* **2026**, *738*, 124761. [\[CrossRef\]](#)
142. Fan, X.; Wei, G.; Quan, X. Carbon Nanomaterial-Based Membranes for Water and Wastewater Treatment under Electrochemical Assistance. *Environ. Sci. Nano* **2023**, *10*, 11–40. [\[CrossRef\]](#)
143. Lee, J.H.; Yun, E.-T.; Ham, S.-Y.; Kim, H.-S.; Sun, P.-F.; Park, H.-D. Electrically Conductive Carbon Nanotube/Graphene Composite Membrane for Self-Cleaning of Biofouling via Bubble Generation. *Desalination* **2022**, *535*, 115841. [\[CrossRef\]](#)
144. Jiang, L.; Rastgar, M.; Wang, C.; Ke, S.; He, L.; Chen, X.; Song, Y.; He, C.; Wang, J.; Sadrzadeh, M. Robust PANI-Entangled CNTs Electro-Responsive Membranes for Enhanced In-Situ Generation of H₂O₂ and Effective Separation of Charged Contaminants. *Sep. Purif. Technol.* **2022**, *303*, 122274. [\[CrossRef\]](#)
145. Lou, M.; Zhu, X.; Fang, X.; Liu, Y.; Li, F. Interception of Volatile Organic Compounds through CNT Electrochemistry of Electrified Membrane Surface during Membrane Distillation. *Sep. Purif. Technol.* **2022**, *297*, 121380. [\[CrossRef\]](#)
146. Zhang, Y.; Farnood, R. A Joule-Heated PTFE-CNT Composite Membrane Fabricated by Solution Blow Spinning for Enhanced Ammonia Recovery. *Sep. Purif. Technol.* **2026**, *382*, 135660. [\[CrossRef\]](#)
147. Lin, Y.-L.; Zheng, N.-Y.; Lin, J.-Y.; Nguyen, N.H. Innovative PANI Composite Modified Conductive FO Membranes for Electro-Assisted Aquaculture Wastewater Recovery. *J. Water Process Eng.* **2026**, *87*, 110068. [\[CrossRef\]](#)
148. Lu, C.; Ren, H.; Sun, J.; Wu, Y.; Chen, Z.; Hu, C.; Qu, J. Facile Fabrication of Electrically Responsive Polypyrrole Membrane to Synergistically Improve Anti-Fouling and Separation Performance. *J. Membr. Sci.* **2025**, *717*, 123598. [\[CrossRef\]](#)
149. Gong, W.; Lu, J.; Guo, X.; Xue, M.; Zhao, Y.; Tong, L.; Yu, Z.; Zheng, K.; Wang, Z.; Xu, D.; et al. Electrochemical OCNT-PPy Membrane Achieving High-Efficiency Ammonia Nitrogen Removal and Enhanced Antifouling Performance: Interface Design and Removal Mechanism. *J. Membr. Sci.* **2026**, *754*, 125677. [\[CrossRef\]](#)
150. Jia, T.-Z.; Feng, R.; Cui, C.; Chen, Q.; Cseri, L.; Zhou, R.-F.; Szekely, G.; Cao, X.-L.; Sun, S.-P. Conductive Nanofiltration Membranes via in Situ PEDOT-Polymerization for Electro-Assisted Membrane Fouling Mitigation. *Water Res.* **2024**, *252*, 121251. [\[CrossRef\]](#) [\[PubMed\]](#)
151. Gao, F.; Li, X.; Shi, W.; Wang, Z. Highly Selective Recovery of Phosphorus from Wastewater via Capacitive Deionization Enabled by Ferrocene-Polyaniline-Functionalized Carbon Nanotube Electrodes. *ACS Appl. Mater. Interfaces* **2022**, *14*, 31962–31972. [\[CrossRef\]](#) [\[PubMed\]](#)
152. Benkhaya, S.; Zhou, Z.; Xiao, Y. Synthesis of a Novel Hybrid Nanofiltration Membrane by Incorporating Functionalized Multiwall Carbon Nanotubes Doped with Silver and NaCl-Polyethersulfone for Efficient Volatile Fatty Acids Rejection. *J. Environ. Chem. Eng.* **2025**, *13*, 115643. [\[CrossRef\]](#)
153. Liu, T.; Qin, H.; Wang, S.; Chen, S.; Qiao, S.; Quan, X. Electrically Conductive Membrane-Based Anammox MBR with Electrochemical Assistance: An Effective Strategy for Simultaneous Mitigation of Membrane Fouling and Enhancement of Nitrogen Removal. *Water Res.* **2026**, *288*, 124636. [\[CrossRef\]](#) [\[PubMed\]](#)
154. Xu, L.; Liu, S.; Zhao, S.; Li, K.; Cao, A.; Wang, J. A Novel Electrocoagulation-Membrane Stripping Hybrid System for Simultaneous Ammonia Recovery and Contaminant Removal. *Sep. Purif. Technol.* **2022**, *296*, 121377. [\[CrossRef\]](#)
155. Yue, C.; Gan, S.; Yan, Z.; Su, B.; Liu, K.; Xia, F.; Li, H.; Zhu, L.; Xue, Q.; Zhang, J. Electro-Driven Pore Expansion of PH-Responsive Membranes to Enhance Antifouling Performance for Efficient Oil-Water Separation. *J. Membr. Sci.* **2025**, *734*, 124390. [\[CrossRef\]](#)
156. Uredat, S.; Gujare, A.; Runge, J.; Truzzolillo, D.; Oberdisse, J.; Hellweg, T. A Review of Stimuli-Responsive Polymer-Based Gating Membranes. *Phys. Chem. Chem. Phys.* **2024**, *26*, 2732–2744. [\[CrossRef\]](#) [\[PubMed\]](#)
157. Mumtaz, F.; Faraz, M.; Balakrishnan, H.K.; Nair, R.; Dumée, L.F. Stimuli-Responsive Membranes—Mechanisms, Materials and Future Directions. *npj Clean Water* **2025**, *9*, 1. [\[CrossRef\]](#)
158. Huang, T.; Su, Z.; Hou, K.; Zeng, J.; Zhou, H.; Zhang, L.; Nunes, S.P. Advanced Stimuli-Responsive Membranes for Smart Separation. *Chem. Soc. Rev.* **2023**, *52*, 4173–4207. [\[CrossRef\]](#) [\[PubMed\]](#)
159. Hosseinzadeh, A.; Ranjbar, P.R.; Bozorg, A. PH-Responsive P(AA-b-SBMA)-Grafted Magnetic GO High-Performance Ultrafiltration Membrane with Improved Antifouling Tendency and Cleaning Efficiency. *Desalination* **2024**, *574*, 117299. [\[CrossRef\]](#)

160. Li, F.; Liang, H.; Shan, J.; Zhang, A.; Lou, H.; Tang, Y. Lignin-Grafted Quaternary Ammonium Phosphate with Temperature and PH Responsive Behavior for Improved Enzymatic Hydrolysis and Cellulase Recovery. *Int. J. Biol. Macromol.* **2023**, *234*, 123779. [[CrossRef](#)] [[PubMed](#)]
161. Lu, L.; Chen, Y.; Chen, C.; Li, L.; Li, B.; Zhao, L.; Shen, L.; Lin, H. Electrically Responsive Reduced Graphene Oxide Membrane with Switchable Nanochannels for Graded Molecular Separation. *J. Membr. Sci.* **2026**, *751*, 125530. [[CrossRef](#)]
162. Zhu, X.; Jassby, D. Electroactive Membranes for Water Treatment: Enhanced Treatment Functionalities, Energy Considerations, and Future Challenges. *Acc. Chem. Res.* **2019**, *52*, 1177–1186. [[CrossRef](#)] [[PubMed](#)]
163. Chen, H.; Yang, F.; Wang, Q.; Zheng, T.; Zhou, R.; Wu, C.; Jin, Y. Fouling Mechanisms in the Clarification of 1,3-Propanediol Fermentation Broths by Membrane Processes. *Membranes* **2025**, *15*, 276. [[CrossRef](#)] [[PubMed](#)]
164. Tomczak, W.; Gryta, M. Microfiltration of Post-Fermentation Broths: Long-Term Studies on the Use of Modules with Polymeric Membranes. *Membranes* **2025**, *15*, 345. [[CrossRef](#)] [[PubMed](#)]
165. Blankert, B.; Van der Bruggen, B.; Childress, A.E.; Ghaffour, N.; Vrouwenvelder, J.S. Potential Pitfalls in Membrane Fouling Evaluation: Merits of Data Representation as Resistance Instead of Flux Decline in Membrane Filtration. *Membranes* **2021**, *11*, 460. [[CrossRef](#)] [[PubMed](#)]
166. Zhang, W.; Luo, J.; Ding, L.; Jaffrin, M.Y. A Review on Flux Decline Control Strategies in Pressure-Driven Membrane Processes. *Ind. Eng. Chem. Res.* **2015**, *54*, 2843–2861. [[CrossRef](#)]
167. Xu, L.; Zhang, Y.; Li, T.; Peng, S.; Wu, D. Simultaneous Desalination and Molecular Resource Recovery from Wastewater Using an Electrical Separation System Integrated with a Supporting Liquid Membrane. *Water Res.* **2023**, *246*, 120706. [[CrossRef](#)] [[PubMed](#)]
168. Bak, C.; Yun, Y.-M.; Kim, J.-H.; Kang, S. Electrodialytic Separation of Volatile Fatty Acids from Hydrogen Fermented Food Wastes. *Int. J. Hydrogen Energy* **2019**, *44*, 3356–3362. [[CrossRef](#)]
169. Haflich, H.M.; Singleton, J.W.; Coronell, O. Relative Contributions of Mobility and Partitioning to Volatile Fatty Acid Flux during Electrodialysis. *J. Membr. Sci.* **2024**, *711*, 123204. [[CrossRef](#)] [[PubMed](#)]
170. He, J.; Liu, W.; Hao, J.; Ma, X.; Zheng, Z.; Fang, Y.; Liang, Y.; Tian, Z.; Sun, L.; Li, C.; et al. Bipolar Membrane Electrodialysis for Direct Conversion of L-Ornithine Monohydrochloride to L-Ornithine. *Int. J. Mol. Sci.* **2023**, *24*, 13174. [[CrossRef](#)] [[PubMed](#)]
171. Rendi, O.M.K.; Gironès, M.; Wiratha, W.; Nijmeijer, K. On the Isolation of Single Basic Amino Acids with Electrodialysis for the Production of Biobased Chemicals. *Ind. Eng. Chem. Res.* **2013**, *52*, 1069–1078. [[CrossRef](#)]
172. Buehler, E.A.; Mesbah, A. Kinetic Study of Acetone-Butanol-Ethanol Fermentation in Continuous Culture. *PLoS ONE* **2016**, *11*, e0158243. [[CrossRef](#)] [[PubMed](#)]
173. Liao, C.; Seo, S.-O.; Celik, V.; Liu, H.; Kong, W.; Wang, Y.; Blaschek, H.; Jin, Y.-S.; Lu, T. Integrated, Systems Metabolic Picture of Acetone-Butanol-Ethanol Fermentation by *Clostridium Acetobutylicum*. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 8505–8510. [[CrossRef](#)] [[PubMed](#)]
174. Guo, Y.; Liu, Y.; Guan, M.; Tang, H.; Wang, Z.; Lin, L.; Pang, H. Production of Butanol from Lignocellulosic Biomass: Recent Advances, Challenges, and Prospects. *RSC Adv.* **2022**, *12*, 18848–18863. [[CrossRef](#)] [[PubMed](#)]
175. Birgen, C.; Dürre, P.; Preisig, H.A.; Wentzel, A. Butanol Production from Lignocellulosic Biomass: Revisiting Fermentation Performance Indicators with Exploratory Data Analysis. *Biotechnol. Biofuels* **2019**, *12*, 167. [[CrossRef](#)] [[PubMed](#)]
176. Paltrinieri, L.; Huerta, E.; Puts, T.; van Baak, W.; Verver, A.B.; Sudhölter, E.J.R.; de Smet, L.C.P.M. Functionalized Anion-Exchange Membranes Facilitate Electrodialysis of Citrate and Phosphate from Model Dairy Wastewater. *Environ. Sci. Technol.* **2019**, *53*, 2396–2404. [[CrossRef](#)] [[PubMed](#)]
177. Zhang, Y.; Van der Bruggen, B.; Pinoy, L.; Meesschaert, B. Separation of Nutrient Ions and Organic Compounds from Salts in RO Concentrates by Standard and Monovalent Selective Ion-Exchange Membranes Used in Electrodialysis. *J. Membr. Sci.* **2009**, *332*, 104–112. [[CrossRef](#)]
178. Cecconi, F.; Pifer, L.; Sabba, F.; Downing, L. Improving Carbon Management through Maximizing Hydrolysis and Fermentation at Water Resource Recovery Facilities. *Front. Environ. Eng.* **2024**, *3*, 1378621. [[CrossRef](#)]
179. Molinos-Senante, M.; Sala-Garrido, R.; Iftimi, A. Energy Intensity Modeling for Wastewater Treatment Technologies. *Sci. Total Environ.* **2018**, *630*, 1565–1572. [[CrossRef](#)] [[PubMed](#)]
180. Tran, Q.; Garcia-Jaramillo, M.; Schindler, J.; Eness, A.; Bryla, D.R.; Patel, H.; Navab-Daneshmand, T.; Jin, X. Sustainable Nutrient Water Recovery by a Hybrid Electrodialysis (ED)—Forward Osmosis (FO) Process for Agricultural Application. *J. Environ. Chem. Eng.* **2024**, *12*, 112091. [[CrossRef](#)]
181. Rajaniemi, K.; Hu, T.; Nurmesniemi, E.T.; Tuomikoski, S.; Lassi, U. Phosphate and Ammonium Removal from Water through Electrochemical and Chemical Precipitation of Struvite. *Processes* **2021**, *9*, 150. [[CrossRef](#)]
182. Thompson Brewster, E.; Ward, A.J.; Mehta, C.M.; Radjenovic, J.; Batstone, D.J. Predicting Scale Formation during Electrodialytic Nutrient Recovery. *Water Res.* **2017**, *110*, 202–210. [[CrossRef](#)] [[PubMed](#)]
183. Pan, W.; Li, K.; Zhang, J.; Duan, Y.; Wang, R.; Dykstra, J.E.; Elimelech, M. Inorganic Scaling in Electrodialysis: Mechanistic Insights and Impact on Energy Efficiency and Ion Selectivity. *Environ. Sci. Technol.* **2026**, *60*, 10298–10308. [[CrossRef](#)] [[PubMed](#)]

184. Kumar, A.; Udugama, I.A.; Gargalo, C.L.; Gernaey, K.V. Why Is Batch Processing Still Dominating the Biologics Landscape? Towards an Integrated Continuous Bioprocessing Alternative. *Processes* **2020**, *8*, 1641. [\[CrossRef\]](#)
185. São Pedro, M.N.; Silva, T.C.; Patil, R.; Ottens, M. White Paper on High-throughput Process Development for Integrated Continuous Biomanufacturing. *Biotechnol. Bioeng.* **2021**, *118*, 3275–3286. [\[CrossRef\]](#) [\[PubMed\]](#)
186. Goren, A.Y.; Dincer, I.; Khalvati, A. A New Electro-Biomembrane Integrated Renewable-Based System to Produce Power, Fresh Water and Hydrogen for Sustainable Communities. *Sustain. Cities Soc.* **2025**, *120*, 106156. [\[CrossRef\]](#)
187. He, L.; Ma, J.; Lu, H.; Li, Q.; Liang, T.; Shang, J. Recovery of Active Proteins from Whey via a Novel Hybrid Process of Chitosan Extraction and Electrodialysis with Ultrafiltration Membrane. *Chem. Eng. Sci.* **2026**, *330*, 123849. [\[CrossRef\]](#)
188. Mutahi, G.; van Lier, J.B.; Spanjers, H. Leveraging Organic Acids in Bipolar Membrane Electrodialysis (BPMED) Can Enhance Ammonia Recovery from Scrubber Effluents. *Water Res.* **2024**, *265*, 122296. [\[CrossRef\]](#) [\[PubMed\]](#)
189. Geoffroy, T.R.; Bernier, M.E.; Thibodeau, J.; Francezon, N.; Beaulieu, L.; Mikhaylin, S.; Langevin, M.E.; Lutin, F.; Bazinet, L. Semi-Industrial Scale-up of EDUF Technology for the Electroseparation of Bioactive Cationic Peptides: Impact of Process Parameters and Cell Configurations on Eco-Efficiency. *J. Membr. Sci.* **2022**, *641*, 119856. [\[CrossRef\]](#)
190. Dowlatshah, S.; Hansen, F.A.; Zhou, C.; Ramos-Payán, M.; Halvorsen, T.G.; Pedersen-Bjergaard, S. Electromembrane Extraction of Peptides Based on Hydrogen Bond Interactions. *Anal. Chim. Acta* **2023**, *1275*, 341610. [\[CrossRef\]](#) [\[PubMed\]](#)
191. Dong, H.; Laguna, C.M.; Liu, M.J.; Guo, J.; Tarpeh, W.A. Electrified Ion Exchange Enabled by Water Dissociation in Bipolar Membranes for Nitrogen Recovery from Source-Separated Urine. *Environ. Sci. Technol.* **2022**, *56*, 16134–16143. [\[CrossRef\]](#) [\[PubMed\]](#)
192. Liu, Q.; Zhang, C.; Lei, Y.; Wang, S.; Liu, Y.; Xu, X. A Continuous Flow-Electrode Capacitive Deionization System for Efficient Ammonia-Nitrogen Recovery and Enrichment from Wastewater. *J. Environ. Chem. Eng.* **2026**, *14*, 121996. [\[CrossRef\]](#)
193. Zhu, C.; Niu, Q.; Liu, D.; Wu, J.; Hao, Y.; Jiang, B. Integrating Divided Electrolysis-Microfiltration Process for Energy-Efficient Phosphorus Recovery in the Form of Calcium Phosphate. *Sep. Purif. Technol.* **2022**, *301*, 121922. [\[CrossRef\]](#)
194. Lameloise, M.-L.; Lewandowski, R. Recovering L-Malic Acid from a Beverage Industry Waste Water: Experimental Study of the Conversion Stage Using Bipolar Membrane Electrodialysis. *J. Membr. Sci.* **2012**, *403–404*, 196–202. [\[CrossRef\]](#)
195. Prochaska, K.; Woźniak-Budych, M.J. Recovery of Fumaric Acid from Fermentation Broth Using Bipolar Electrodialysis. *J. Membr. Sci.* **2014**, *469*, 428–435. [\[CrossRef\]](#)
196. Lin, X.; Pan, J.; Zhou, M.; Xu, Y.; Lin, J.; Shen, J.; Gao, C.; Van der Bruggen, B. Extraction of Amphoteric Amino Acid by Bipolar Membrane Electrodialysis: Methionine Acid as a Case Study. *Ind. Eng. Chem. Res.* **2016**, *55*, 2813–2820. [\[CrossRef\]](#)
197. Zhang, H.; Du, L.; Xing, J.; Wei, G.; Quan, X. Electro-Conductive Crosslinked Polyaniline/Carbon Nanotube Nanofiltration Membrane for Electro-Enhanced Removal of Bisphenol A. *Front. Environ. Sci. Eng.* **2023**, *17*, 59. [\[CrossRef\]](#)
198. Tian, K.; Xu, X.; Yin, Z.; Liu, Y.; Zhu, Y.; Li, F.; Wen, T.; Yang, W. Sustainable Control of Organic-Inorganic Combined Fouling of Electroactive Ultrafiltration Membrane during Electrocatalytic-Driven Self-Cleaning Process: Mechanism and Implications. *J. Water Process Eng.* **2024**, *65*, 105751. [\[CrossRef\]](#)
199. Chen, D.; Kim, J.-T.; Chamorro, L.P.; Timperman, A.T. Exceeding Ohmic Scaling by More than One Order of Magnitude with a 3D Ion Concentration Polarization System. *Lab Chip* **2021**, *21*, 3094–3104. [\[CrossRef\]](#) [\[PubMed\]](#)
200. Arunachalam, M.; Yoo, Y.; Al-Ghamdi, A.S.; Park, H.; Han, D.S. Integrating Green Hydrogen Production with Renewable Energy-Powered Desalination: An Analysis of CAPEX Implications and Operational Strategies. *Int. J. Hydrogen Energy* **2024**, *84*, 344–355. [\[CrossRef\]](#)
201. Hamdan, S.; Al-Ghafri, B.; Al-Obaidani, S.; Tarboush, B.A.; Al-Sabahi, J.; Al-Abri, M. Dairy Wastewater Treatment with Direct-Contact Membrane Distillation in Oman. *Desalination Water Treat.* **2024**, *320*, 100672. [\[CrossRef\]](#)
202. Leaper, S.; Abdel-Karim, A.; Gorgojo, P. The Use of Carbon Nanomaterials in Membrane Distillation Membranes: A Review. *Front. Chem. Sci. Eng.* **2021**, *15*, 755–774. [\[CrossRef\]](#)
203. Zhao, W.; Jiang, H.; Dong, W.; Liang, Q.; Yan, B.; Zhang, Y. Elevated Caproic Acid Production from One-Stage Anaerobic Fermentation of Organic Waste and Its Selective Recovery by Electro-Membrane Process. *Bioresour. Technol.* **2024**, *399*, 130647. [\[CrossRef\]](#) [\[PubMed\]](#)
204. Liu, F.; Moustafa, H.; He, Z. Simultaneous Recovery of Nitrogen and Phosphorus from Actual Digester Centrate in an Electrochemical Membrane System. *Resour. Conserv. Recycl.* **2024**, *203*, 107463. [\[CrossRef\]](#)
205. Liu, H.; Foo, Z.H.; She, Q. The Potential of Electrodialysis with Mediating Solution (EDM) for Eliminating Alkaline Scaling: Experimental Validation and Mechanistic Elucidation. *Environ. Sci. Technol.* **2025**, *59*, 6307–6318. [\[CrossRef\]](#) [\[PubMed\]](#)
206. Ledingham, J.; Howse, J.R.; Campbell, A.N.; Veen, B.i.; Keyzer, L.; Sedransk Campbell, K.L. Experimental Validation of the Presence of Flow Maldistribution in Electrodialysis Stacks and Its Effect on the Limiting Current Density. *J. Membr. Sci.* **2025**, *716*, 123494. [\[CrossRef\]](#)
207. Li, N.N. Scale-up of Thin-Film Composite Membranes: Interdisciplinary Considerations for Commercialization. *J. Membr. Sci.* **2026**, *737*, 124777. [\[CrossRef\]](#)

208. Beuscher, U.; Kappert, E.J.; Wijmans, J.G. Membrane Research beyond Materials Science. *J. Membr. Sci.* **2022**, *643*, 119902. [[CrossRef](#)]
209. Asunis, F.; De Gioannis, G.; Dessì, P.; Isipato, M.; Lens, P.N.L.; Muntoni, A.; Poletti, A.; Pomi, R.; Rossi, A.; Spiga, D. The Dairy Biorefinery: Integrating Treatment Processes for Cheese Whey Valorisation. *J. Environ. Manag.* **2020**, *276*, 111240. [[CrossRef](#)] [[PubMed](#)]
210. Khandelwal, N.; Kumari, S.; Poduval, S.; Behera, S.K.; Kumar, A.; Gedam, V.V. Life-Cycle Assessment of Three Biorefinery Pathways across Different Generations. *Sci. Rep.* **2025**, *15*, 13135. [[CrossRef](#)] [[PubMed](#)]
211. Mallapragada, D.S.; Dvorkin, Y.; Modestino, M.A.; Esposito, D.V.; Smith, W.A.; Hodge, B.-M.; Harold, M.P.; Donnelly, V.M.; Nuz, A.; Bloomquist, C.; et al. Decarbonization of the Chemical Industry through Electrification: Barriers and Opportunities. *Joule* **2023**, *7*, 23–41. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.