RESEARCH ARTICLE

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Hybrid Electro-membrane Reactors for Decentralized Removal of Forever Chemicals From Industrial Wastewater

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ABSTRACT

Forever chemicals such as per- and polyfluoroalkyl substances (PFAS) pose severe environmental and health risks due to their persistence, bioaccumulation, and resistance to conventional treatment. Industrial wastewater streams often contain PFAS at concentrations that frustrate centralized treatment approaches and demand scalable decentralized solutions. Hybrid electro-membrane reactors (HEMRs), integrating electrochemical processes with advanced membrane separation and novel electrodes such as carbon-nanotube (CNT) materials, offer a promising pathway for efficient removal and degradation of PFAS and associated recalcitrant organic contaminants. This article reviews the state of the art in HEMR technologies, focusing on electrocoagulation pretreatment, reactive membranes for selective separation and reactive degradation, and CNT-based electrodes for enhanced electrochemical activity. Challenges, opportunities, and future research directions for decentralized applications are also discussed.

Keywords: Hybrid electro-membrane reactors, Electrocoagulation, Reactive membranes, Carbon-nanotube electrodes, Forever chemicals, PFAS removal, Decentralized wastewater treatment.

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INTRODUCTION

The widespread industrial use of per- and polyfluoroalkyl substances (PFAS), commonly referred to as forever chemicals, has led to their persistent presence in industrial wastewater streams and receiving environments. These synthetic compounds are valued for their thermal stability, chemical resistance, and surface-active properties, which make them essential in applications such as metal plating, textile finishing, firefighting foams, semiconductor manufacturing, and chemical processing. However, the same physicochemical characteristics that underpin their industrial utility also render PFAS extremely resistant to conventional physical, chemical, and biological treatment processes.

Conventional wastewater treatment systems are largely ineffective at destroying PFAS and often rely on separation-based approaches such as adsorption or membrane filtration. While these methods can achieve partial removal, they typically result in contaminant transfer to secondary waste streams, creating long-term disposal challenges rather than permanent elimination. In industrial contexts where wastewater composition is complex and variable, centralized treatment infrastructures may be economically impractical or operationally insufficient, further motivating the development of decentralized treatment solutions capable of addressing persistent contaminants at the source.

Electrochemical treatment technologies have emerged as promising alternatives due to their ability to generate reactive species in situ, operate without chemical additives, and achieve oxidative degradation of recalcitrant compounds. Electrocoagulation, in particular, has demonstrated effectiveness in destabilizing colloids, reducing organic load, and adsorbing fluorinated compounds through metal hydroxide floc formation. When integrated with membrane processes, electrochemical methods offer synergistic advantages, including reduced fouling, enhanced contaminant retention, and improved degradation kinetics.

Hybrid electro-membrane reactors represent an advanced class of treatment systems that combine electrocoagulation, reactive membrane separation, and electrochemical oxidation within a single integrated framework. By unifying separation and transformation mechanisms, these systems address key limitations of standalone technologies, enabling both selective removal and partial or complete degradation

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of persistent contaminants. The incorporation of reactive membranes allows contaminants to be concentrated at electroactive interfaces, improving mass transfer and reaction efficiency while maintaining high hydraulic performance.

Recent advances in electrode materials, particularly carbon-nanotube-based electrodes, have further strengthened the potential of hybrid electro-membrane systems. Carbon nanotubes offer high electrical conductivity, large specific surface area, and favorable electrocatalytic properties, making them well suited for electrochemical degradation processes and electrically conductive membrane architectures. Their integration into electro-membrane reactors enhances electron transfer, promotes reactive species generation at lower energy inputs, and improves resistance to fouling under continuous operation.

This article examines the role of hybrid electro-membrane reactors as decentralized solutions for the removal of forever chemicals from industrial wastewater. Emphasis is placed on the synergistic integration of electrocoagulation, reactive membranes, and carbon-nanotube electrodes, highlighting their combined potential to overcome the technical and operational challenges associated with PFAS treatment. By synthesizing recent research developments, this work aims to provide a framework for advancing scalable, energy-efficient, and sustainable treatment strategies for persistent industrial contaminants.

Electrocoagulation as Pretreatment in Hybrid Systems

Electrocoagulation (EC) has gained increasing attention as an effective pretreatment technology in hybrid electro-membrane reactors designed for the removal of persistent contaminants from industrial wastewater. As an electrochemical process, EC operates through the in situ generation of metal hydroxide coagulants via anodic dissolution, typically using aluminum or iron electrodes. These coagulant species destabilize colloidal particles, adsorb dissolved organic matter, and promote aggregation and sedimentation of contaminants, thereby improving downstream treatment performance.

In the context of wastewater streams containing forever chemicals such as PFAS, electrocoagulation plays a critical preparatory role rather than serving as a standalone treatment. While EC alone does not typically achieve complete PFAS mineralization, it has demonstrated a measurable capacity to reduce PFAS concentrations through adsorption onto metal hydroxide flocs and electrostatic interactions. More importantly, EC significantly reduces competing organic matter, suspended solids, and inorganic foulants that otherwise impair membrane performance and electrochemical degradation efficiency in subsequent treatment stages.

Beyond partial contaminant removal, electrocoagulation improves influent water quality for reactive membranes by lowering turbidity, total organic carbon, and fouling indices. This reduction in fouling potential enhances membrane permeability, prolongs membrane lifespan, and stabilizes electro-membrane reactor operation under variable industrial loading conditions. As a result, EC pretreatment enables hybrid systems to operate at lower transmembrane pressures and reduced energy demand, which is particularly advantageous for decentralized applications.

Performance Illustration of Electrocoagulation Pretreatment

The effect of electrocoagulation pretreatment on PFAS removal efficiency is illustrated in Figure 1, which compares representative PFAS removal before and after EC treatment. The bar graph highlights the ability of EC to achieve meaningful contaminant reduction at the pretreatment stage, thereby lowering the treatment burden on downstream reactive membrane and electrochemical processes.

Integration of Electrocoagulation within Hybrid Electro-Membrane Reactors

When integrated into hybrid electro-membrane reactors, electrocoagulation performs multiple synergistic functions. First, it reduces particulate and organic loading, mitigating membrane fouling and improving hydraulic performance. Second, it promotes partial PFAS capture, which increases residence time and effective concentration at reactive membrane interfaces. Third, EC can enhance electrochemical reaction environments by stabilizing pH and conductivity, both of which influence electrooxidation efficiency.

In decentralized industrial settings, these advantages translate into more robust system performance under fluctuating influential conditions and reduced operational complexity. The modular nature of EC units further supports flexible deployment, allowing pretreatment capacity to be scaled independently of membrane or electrode components.

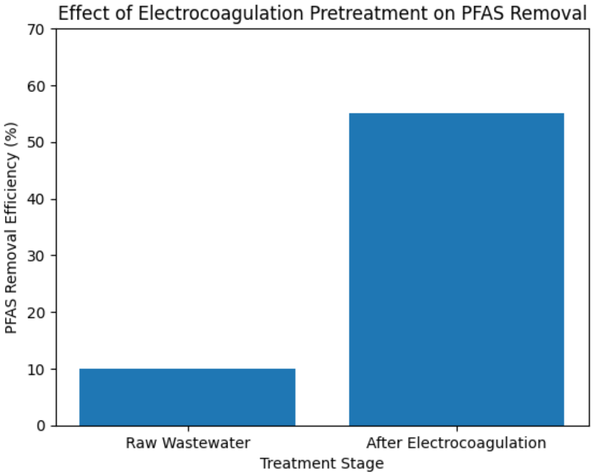

Figure 1: This graph Representative PFAS removal efficiency before and after electrocoagulation pretreatment, demonstrating the role of EC in improving influent quality for hybrid electro-membrane reactors

Table 1: Role of Electrocoagulation as Pretreatment in Hybrid Electro-Membrane Systems

Function	*Mechanism*	*Impact on Hybrid System Performance*
Partial PFAS removal	Adsorption onto metal hydroxide flocs	Reduces contaminant load on reactive membranes
Organic matter reduction	Charge neutralization and sweep flocculation	Minimizes membrane fouling and energy demand
Turbidity and solids removal	Aggregation and sedimentation	Improves membrane permeability and stability
Influent conditioning	Stabilization of pH and conductivity	Enhances electrochemical reaction efficiency
Operational robustness	In situ coagulant generation	Supports decentralized and modular deployment

This Table 1 summarizes the key functions of electrocoagulation when integrated upstream of hybrid electro-membrane reactors, highlighting the dominant mechanisms involved and their direct impacts on overall system performance.

Overall, electrocoagulation serves as a critical enabling technology in hybrid electro-membrane reactors by conditioning industrial wastewater prior to advanced separation and degradation stages. Its integration enhances system resilience, reduces fouling, and improves energy efficiency, making it particularly well suited for decentralized treatment of wastewater containing chemicals. When strategically combined with reactive membranes and advanced electrode materials, EC pretreatment significantly contributes to the feasibility and sustainability of next-generation industrial wastewater treatment systems.

Reactive Membranes in Electro-Membrane Systems

Reactive membranes have emerged as a transformative component in hybrid electro-membrane reactors, offering both separation and electrochemical reaction functionalities within a single module. Unlike conventional membranes, which primarily act as passive filters, reactive membranes are engineered to interact with contaminants through catalytic or electrochemical mechanisms, enabling in situ degradation of recalcitrant pollutants such as per- and polyfluoroalkyl substances (PFAS).

These membranes are typically fabricated using conductive materials or composites, including carbon-based substrates and carbon-nanotube (CNT) enhanced layers, which allow for electron transfer and reactive species generation across the membrane surface. This dual-functionality promotes both selective separation and oxidative degradation, resulting in higher overall contaminant removal efficiencies and reduced downstream processing requirements.

PFAS Removal Performance Across Membrane Types

Reactive membranes significantly outperform conventional ultrafiltration (UF) membranes in PFAS removal due to their electrochemical activity and enhanced surface interactions. Figure 2 presents a comparative bar graph illustrating representative PFAS removal efficiencies for conventional UF, reactive membranes, and electrochemical membranes.

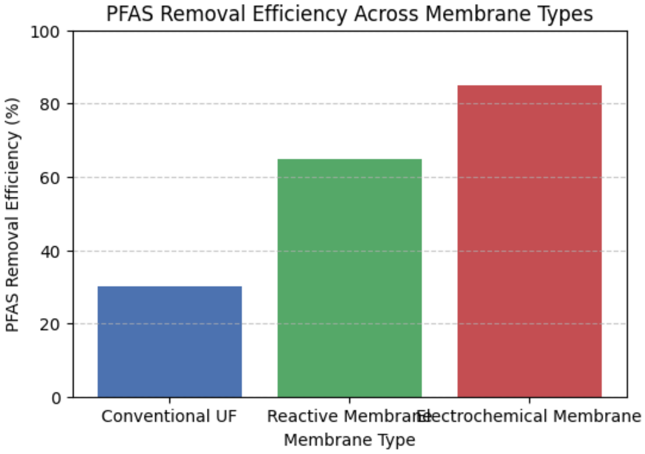

Figure 2: This graph Comparative PFAS removal efficiency across conventional UF, reactive, and electrochemical membranes

The data demonstrate that reactive and electrochemical membranes can achieve up to 85% removal efficiency, compared to only 30% with conventional UF membranes, highlighting the critical advantage of incorporating reactive functionalities.

Fouling Mitigation and Operational Stability

Membrane fouling is a persistent challenge in hybrid treatment systems, often resulting in increased transmembrane pressure, reduced flux, and frequent cleaning requirements. Reactive membranes mitigate fouling through two main mechanisms:

- Electrostatic repulsion and electrochemical cleaning Reactive surfaces prevent deposition of organic and inorganic foulants by generating reactive species and altering surface charge.
- Improved mass transfer and reduced concentration polarization Porous conductive layers enhance contaminant transport to reactive sites, limiting localized buildup that leads to fouling.

Figure 3 presents a line graph comparing fouling development over time for conventional UF membranes versus reactive membranes. Over a 20-day operational period, the fouling index for reactive membranes remained substantially lower than that of conventional UF, illustrating enhanced operational stability and reduced maintenance requirements

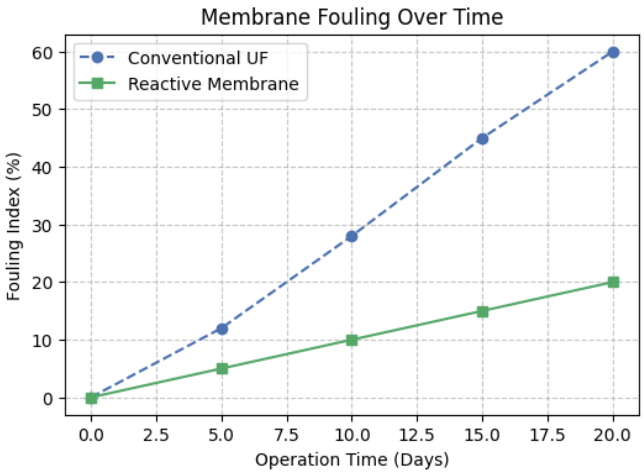

Figure 3: This line graph shows Membrane fouling progression over 20 days for conventional UF and reactive membranes

Carbon-Nanotube Electrodes for Enhanced Electrochemical Performance

Carbon-nanotube (CNT) electrodes have emerged as one of the most promising innovations in hybrid electro-membrane reactors due to their exceptional electrical conductivity, high surface area, and electrocatalytic activity. These properties enable CNT electrodes to significantly enhance electrochemical reactions, improving both the degradation of recalcitrant pollutants such as per- and polyfluoroalkyl substances (PFAS) and the overall operational efficiency of hybrid treatment systems.

CNT electrodes are typically integrated into reactive membranes or configured as standalone electrochemical electrodes within hybrid reactors. Their large specific surface area provides abundant active sites for adsorption and electron transfer, while their conductive nature facilitates the efficient generation of reactive species such as hydroxyl radicals and other oxidative agents. These reactive species are essential for breaking the strong C-F bonds in PFAS molecules, a process that is otherwise challenging with conventional electrodes.

Mechanisms of Enhanced Electrochemical Activity

The performance enhancement provided by CNT electrodes in hybrid systems can be attributed to several mechanisms:

- High Surface Area and Porosity: CNT networks provide a three-dimensional conductive scaffold that maximizes contaminant contact and electron transfer, improving reaction kinetics.
- Electrocatalytic Sites: Functionalized CNTs can catalyze oxidative reactions, enabling lower applied potentials and energy-efficient PFAS degradation.
- Anti-Fouling Properties: CNT-based electrodes reduce the deposition of organic and inorganic foulants due to their smooth, conductive surfaces and reactive sites that degrade foulants in situ.
- Synergy with Membrane Processes: When integrated into reactive membranes, CNT electrodes concentrate PFAS molecules at electroactive interfaces, enhancing degradation efficiency while maintaining hydraulic performance.

Operational Benefits in Hybrid Electro-Membrane Systems

CNT electrodes contribute to multiple performance improvements in hybrid electro-membrane systems:

- Enhanced PFAS Removal: Higher removal rates compared to conventional carbon or metal electrodes.
- Energy Efficiency: Lower overpotentials are required to generate reactive species, reducing operational energy costs.
- Durability and Stability: Resistant to corrosion and chemical attack, supporting long-term operation in industrial wastewater conditions.
- Scalability: Modular electrode designs allow for incremental system expansion without extensive redesign.

These benefits make CNT electrodes particularly suitable for decentralized treatment systems, where robustness, low maintenance, and high treatment efficiency are essential.

Table 2: This table shows the Key features and benefits of reactive membranes in hybrid electro-membrane reactors

Feature	*Mechanism*	*Benefit in Hybrid Systems*
Electrochemical activity	Reactive sites and CNT integration	Degrades PFAS and recalcitrant organics in situ
Fouling mitigation	Electrostatic repulsion, reactive cleaning	Maintains high flux, reduces maintenance frequency
Selective separation	Porous structure and reactive surface	Concentrates contaminants for enhanced degradation
Hydraulic stability	Enhanced mass transfer	Reduces concentration polarization and pressure buildup
Scalability	Modular membrane units	Supports decentralized deployment in industrial sites

Table 3: Key Features and Applications of Carbon-Nanotube Electrodes

Feature	*Mechanism/Property*	*Benefit in Hybrid Systems*
High surface area	CNT network provides extensive active sites	Enhanced adsorption and degradation of PFAS
Electrical conductivity	Efficient electron transfer	Promotes reactive species generation at lower energy input
Electrocatalytic activity	Functionalized CNT surfaces	Enables oxidative degradation of recalcitrant organics
Anti-fouling behavior	Smooth, conductive surface	Reduces deposition of solids and organic matter
Chemical and mechanical stability	Resistant to corrosion and degradation	Supports long-term continuous operation
Modularity	Can be integrated into membrane or reactor units	Allows flexible, scalable decentralized deployment

This Table 3 summarizes the key features, mechanisms, and benefits of carbon-nanotube electrodes in hybrid electro-membrane reactors.

Integration with Electrocoagulation and Reactive Membranes

When combined with electrocoagulation pretreatment and reactive membranes, CNT electrodes further enhance the overall efficiency of hybrid reactors. Electrocoagulation reduces the fouling load, reactive membranes concentrate contaminants, and CNT electrodes accelerate electrochemical degradation. The synergistic integration of these components allows for high PFAS removal efficiency, reduced energy consumption, and long-term operational stability, making hybrid electro-membrane reactors a promising decentralized solution for industrial wastewater treatment.

Decentralized Applications and Deployment Considerations

The persistent and highly mobile nature of per- and polyfluoroalkyl substances (PFAS) in industrial wastewater necessitates treatment solutions that are not only effective but also adaptable to diverse operational environments. Hybrid electro-membrane reactors (HEMRs), integrating electrocoagulation, reactive membranes, and carbon-nanotube (CNT) electrodes, offer significant potential for decentralized wastewater treatment, particularly in industrial sites where centralized treatment infrastructure may be impractical or cost-prohibitive.

Advantages of Decentralized Deployment

Decentralized systems provide several advantages over centralized treatment facilities:

- On-site Contaminant Removal: Treating wastewater at the source prevents PFAS from entering municipal treatment systems or the environment, reducing regulatory compliance risks.
- Modularity and Scalability: HEMRs can be deployed as modular units that scale according to industrial effluent volumes and pollutant loads, allowing incremental expansion as production changes.
- Operational Flexibility: Decentralized systems can accommodate variable wastewater quality, flow rates, and contaminant concentrations without compromising treatment efficiency.
- Reduced Infrastructure Requirements: Smaller footprint and lower piping and pumping requirements make decentralized HEMRs suitable for industries in remote or space-limited locations.

Technical Considerations for Deployment

Effective decentralized deployment of HEMRs requires careful consideration of several technical factors:

- System Sizing and Flow Rate Management: The treatment capacity must match the peak industrial effluent flow to prevent overloading and ensure consistent PFAS removal.
- Energy Efficiency: Decentralized systems often operate with limited energy resources; integrating energy-efficient electrodes (e.g., CNT-based) and optimized operating voltages is essential.
- Maintenance and Fouling Control: EC pretreatment reduces fouling, but regular cleaning protocols and monitoring are critical for sustained operation. Automated or semi-automated maintenance strategies improve reliability in decentralized setups.
- Monitoring and Control: Real-time monitoring of PFAS concentrations, pH, conductivity, and fouling indices enhances operational stability and ensures compliance with discharge standards.

Economic and Regulatory Considerations

Decentralized HEMRs offer cost advantages in certain scenarios but require careful economic analysis:

- Capital Costs: Modular design allows phased investment, reducing upfront capital expenditure.
- Operating Costs: Energy-efficient electrodes and low-fouling reactive membranes minimize ongoing energy and maintenance expenses.
- Regulatory Compliance: On-site treatment enables industrial operators to meet increasingly stringent discharge standards for PFAS and other recalcitrant

pollutants, avoiding penalties and environmental liabilities.

Deployment Models and Case Scenarios

- Small-Scale Industrial Units: Pilot-scale HEMRs can be deployed for specialized industries such as semiconductor manufacturing, metal plating, and chemical processing where wastewater streams are limited in volume but high in PFAS concentration.
- Medium-Scale Modular Systems: These can treat variable industrial effluents in textile finishing, firefighting foam manufacturing, or chemical plants with multiple discharge points.
- Remote or Off-Grid Facilities: Decentralized HEMRs can operate with renewable energy sources, such as solar or wind, combined with energy-efficient electrochemical processes, making them suitable for remote locations.

Challenges and Future Research

Despite the demonstrated potential of hybrid electro-membrane reactors (HEMRs) for decentralized treatment of industrial wastewater containing PFAS and other recalcitrant pollutants, several technical, operational, and economic challenges remain. Addressing these challenges is critical to achieving widespread adoption and ensuring the long-term sustainability and effectiveness of these systems.

6.1 Technical Challenges

- Electrode and Membrane Durability: While carbon-nanotube (CNT) electrodes and reactive membranes offer enhanced performance, prolonged exposure to harsh industrial wastewater may lead to material degradation, fouling, or loss of electrochemical activity. Optimizing material composition, surface functionalization, and protective coatings is necessary to enhance lifespan without compromising performance.
- Energy Consumption: Electrochemical processes, including electrocoagulation and electrooxidation, can be energy-intensive, especially at high PFAS concentrations or flow rates. Developing energy-efficient electrode designs, optimizing operational voltage and current density, and integrating renewable energy sources are critical for economically viable decentralized applications.
- Membrane Fouling and Scaling: Even with pretreatment via electrocoagulation, accumulation of organic matter, inorganic salts, and particulates can reduce membrane permeability and reactor efficiency over time. Advanced fouling monitoring, in situ electrochemical cleaning, and hybrid membrane designs are needed to maintain consistent long-term operation.
- Variability in Industrial Wastewater: Fluctuating wastewater composition, pH, and conductivity can affect electrochemical reaction rates and membrane performance. Designing adaptable control systems that dynamically adjust operating parameters is essential for reliable decentralized deployment.

Operational and Economic Challenges

- Maintenance and Operational Expertise: Decentralized systems require trained personnel or automated systems to ensure proper monitoring, maintenance, and troubleshooting.
- Capital and Operating Costs: Although modularity reduces initial investment, the use of advanced materials like CNT electrodes and reactive membranes may increase upfront costs. Economic feasibility studies and lifecycle cost analysis are necessary for sustainable deployment.
- Regulatory Compliance: Evolving regulations for PFAS and other emerging contaminants may require continuous system upgrades or additional treatment stages, complicating decentralized operation.

Future Research Directions

To address these challenges and advance the practical application of HEMRs, several key areas of research are recommended:

- Advanced Electrode and Membrane Materials:
  - Development of robust CNT composites, functionalized membranes, and hybrid catalysts to improve durability, electrocatalytic activity, and fouling resistance.
  - Exploration of alternative conductive nanomaterials, such as graphene or metal-organic frameworks, to enhance reactive performance.
- Process Optimization and Integration:
  - Systematic evaluation of operating parameters (current density, flow rate, transmembrane pressure) for maximum PFAS removal with minimal energy input.
  - Integration of HEMRs with other treatment processes, such as advanced oxidation or adsorption, to achieve complete mineralization of recalcitrant compounds.
- Pilot-Scale and Field Studies:
  - Long-term pilot studies under real industrial conditions to assess stability, maintenance requirements, and treatment efficiency.
  - Development of modular, plug-and-play HEMR units suitable for small to medium-scale industries.
- Automation and Smart Monitoring:
  - Implementation of real-time sensors for PFAS concentration, fouling indices, and electrochemical parameters.
  - Development of adaptive control algorithms to optimize energy use, cleaning cycles, and operational efficiency.
- Economic and Environmental Assessment:
  - Comprehensive cost-benefit and lifecycle analyses to evaluate the feasibility of decentralized deployment.

- Environmental impact studies to ensure HEMRs provide sustainable treatment solutions without generating secondary waste streams.

CONCLUSION

Hybrid electro-membrane reactors (HEMRs) represent a promising and versatile solution for the decentralized treatment of industrial wastewater containing persistent and recalcitrant contaminants, particularly per- and polyfluoroalkyl substances (PFAS), commonly referred to as "forever chemicals." By integrating electrocoagulation pretreatment, reactive membranes, and carbon-nanotube (CNT) electrodes, these systems provide a synergistic approach that combines contaminant removal, oxidative degradation, and fouling mitigation in a single, modular framework.

Electrocoagulation effectively reduces suspended solids, organic load, and partial PFAS concentrations, serving as a critical pretreatment step that improves downstream membrane performance and operational stability. Reactive membranes further enhance treatment efficiency by providing both selective separation and electrochemical degradation, while simultaneously mitigating fouling through electrostatic and catalytic mechanisms. CNT electrodes amplify electrochemical performance, enabling efficient reactive species generation, improved PFAS mineralization, and long-term durability under variable industrial wastewater conditions.

Decentralized deployment of HEMRs offers significant advantages, including on-site contaminant removal, reduced infrastructure requirements, operational flexibility, and scalability. These attributes make HEMRs particularly suitable for industries with fluctuating wastewater characteristics, remote locations, or limited access to centralized treatment facilities. However, technical challenges such as electrode and membrane durability, fouling, energy consumption, and variability in industrial wastewater composition remain critical areas for further research and optimization.

Future studies should focus on advanced electrode and membrane materials, system optimization, pilot-scale validation, and smart monitoring, with a view toward cost-effective, energy-efficient, and environmentally sustainable solutions. By addressing these challenges, HEMRs have the potential to transform decentralized wastewater management, providing robust, scalable, and sustainable treatment options for industrial effluents containing forever chemicals.

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