

Microbial Electrochemical Systems: Transitioning Wastewater Treatment from Energy Sink to Resource Mine

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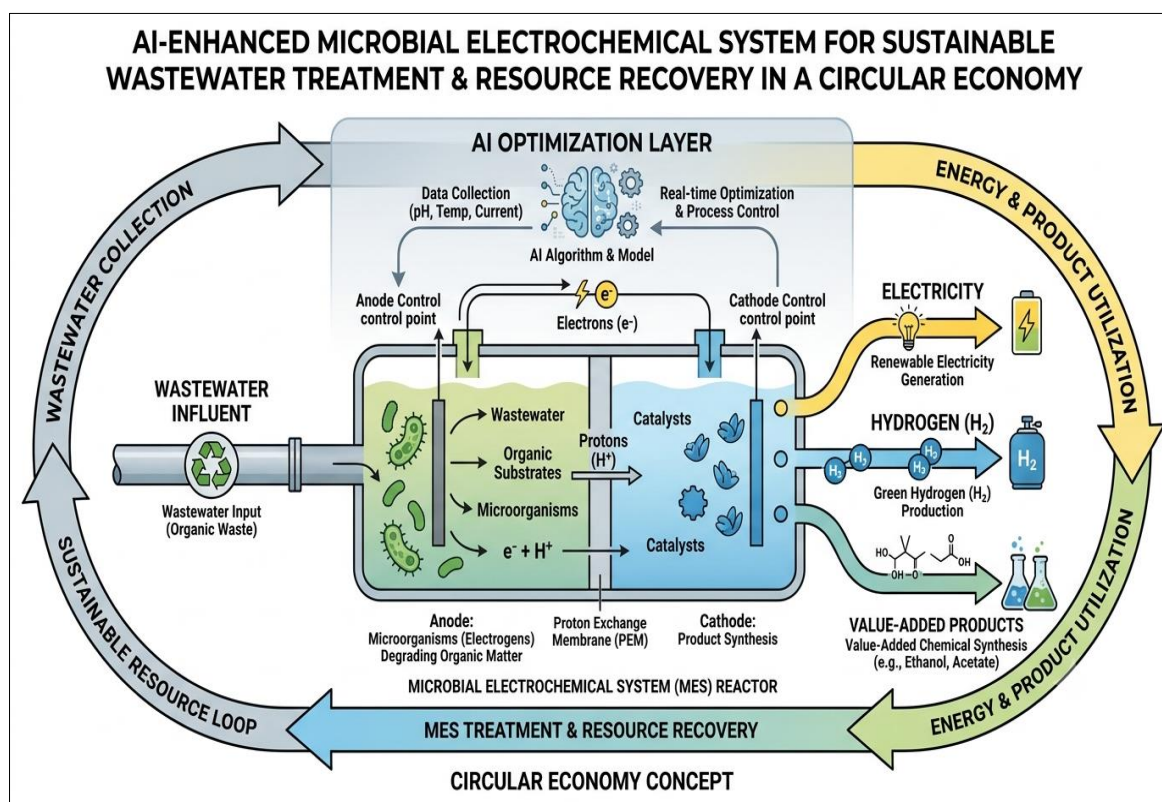
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Abstract



Graphical Abstract

Traditional wastewater treatment infrastructure, heavily reliant on aerobic processes like activated sludge, operates as a significant net energy sink, consuming approximately 1–3% of global electricity production primarily for mechanical aeration. This operational model overlooks the substantial chemical energy (~16.1 kJ/g COD) embedded within organic pollutants. Microbial Electrochemical Systems (MESS) including Microbial Fuel Cells (MFCs) and Microbial Electrolysis Cells (MECs) represent a foundational shift in environmental biotechnology by leveraging electrochemically active bacteria (EAB) for extracellular electron transfer (EET) directly to solid-state electrodes. This article provides a

comprehensive academic review of MES principles, evaluating fundamental thermodynamics, advancements in electrode material engineering, and diverse resource recovery pathways, including direct electricity generation, biohydrogen production, and targeted nutrient mining (e.g., struvite precipitation). Key bottlenecks limiting real-world scalability, such as high internal ohmic resistance, mass-transfer constraints, and capital expenditures, are critically analyzed. We propose a framework for integrating MESs into hybrid treatment trains to achieve process intensification, establishing a pathway for transitioning wastewater management facilities into circular bio-economy "resource mines."

Keywords: Microbial Electrochemical Systems (MES), Wastewater Treatment, Extracellular Electron Transfer (EET), Resource Recovery, Microbial Fuel Cell (MFC), Microbial Electrolysis Cell (MEC), Bioenergy, Nutrient Mining, Circular Economy.

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1. INTRODUCTION

Wastewater as an Untapped Energy Resource

Municipal wastewater contains substantial quantities of chemical energy embedded within biodegradable organic matter. Traditionally, wastewater treatment has been regarded primarily as an environmental protection service aimed at reducing pollutant loads before discharge into receiving water bodies. However, advances in environmental engineering have increasingly highlighted wastewater as a valuable source of recoverable energy and materials. Heidrich *et al.*, reported that the chemical energy content of municipal wastewater significantly exceeds the electrical energy required for its treatment, suggesting that modern wastewater treatment facilities could potentially achieve energy neutrality or even net-positive energy production under optimized operating conditions. This paradigm shift has stimulated growing interest in technologies capable of simultaneously treating wastewater while recovering embedded energy and nutrients.

The energy demands of conventional activated sludge systems remain a major challenge for sustainable wastewater management. Aeration alone typically accounts for 50–70% of total plant electricity consumption. Studies evaluating wastewater treatment facilities across Europe and Asia have demonstrated that improving energy efficiency through process optimization, biogas utilization, and advanced treatment technologies can substantially reduce operational costs and greenhouse gas emissions. For example, analyses of municipal wastewater treatment plants in Poland and other European countries have shown that energy management strategies play a critical role in achieving carbon footprint reduction and operational sustainability (Kłosok-Bazan *et al.*, 2024; Masłoń, 2017; Mielcarek *et al.*, 2024).

Microbial electrochemical systems offer a fundamentally different approach to wastewater treatment by directly harnessing the metabolic activity of microorganisms for energy recovery. Unlike conventional systems that consume energy to remove pollutants, MESs enable microorganisms to transfer electrons generated during organic matter oxidation to electrodes, creating electrical current or driving valuable electrochemical reactions. This capability transforms wastewater from an energy-consuming waste stream into

a renewable resource capable of supporting electricity generation, hydrogen production, nutrient recovery, and carbon capture.

Recent investigations have demonstrated that microbial fuel cells can recover a portion of the energy stored in wastewater while simultaneously achieving substantial organic matter removal. Ge *et al.*, demonstrated efficient electrical energy recovery from wastewater using microbial fuel cell systems, highlighting their potential for decentralized energy production and wastewater treatment integration. Although current power outputs remain insufficient for large-scale grid applications, continued improvements in electrode materials, reactor architectures, and microbial community engineering have steadily enhanced system performance.

Transition from Waste Treatment to Resource Recovery

The evolution of wastewater treatment toward resource recovery represents one of the most significant transformations in environmental engineering over the past two decades. Modern Water Resource Recovery Facilities (WRRFs) are increasingly designed to recover multiple resources simultaneously, including energy, nutrients, reclaimed water, and valuable chemicals. Microbial electrochemical technologies align strongly with this concept because they provide a versatile platform capable of integrating biological degradation processes with electrochemical conversion pathways.

Among the various MES configurations, microbial fuel cells have received considerable attention for electricity generation, whereas microbial electrolysis cells have emerged as promising technologies for sustainable hydrogen production. Microbial desalination cells offer opportunities for simultaneous wastewater treatment and saline water desalination, while microbial electrosynthesis systems facilitate carbon dioxide conversion into value-added chemicals such as acetate, methane, and ethanol. These capabilities position MESs as multifunctional technologies supporting several Sustainable Development Goals (SDGs), including clean water and sanitation, affordable and clean energy, responsible consumption and production, and climate action.

The integration of microbial electrochemical systems with existing treatment technologies has further

expanded their practical applicability. Hybrid systems combining MESs with anaerobic membrane bioreactors, anaerobic digestion units, and advanced nutrient recovery processes have demonstrated enhanced treatment efficiency and improved energy balances. Ren *et al.*, reported that coupling microbial fuel cells with anaerobic fluidized bed membrane bioreactors significantly improved wastewater treatment performance while facilitating energy recovery. Such hybrid approaches are increasingly viewed as a realistic pathway toward full-scale implementation.

Pilot-Scale Progress and Commercialization Challenges

Despite remarkable advances at laboratory scale, the transition of MES technologies toward pilot-scale and commercial deployment remains challenging. Recent reviews emphasize that performance metrics observed in laboratory reactors frequently decline when systems are scaled up due to increased internal resistance, electrode spacing limitations, membrane fouling, mass transfer constraints, and operational complexity. Li *et al.*, (2024) highlighted recent advances in separators, pilot-scale reactor design, and practical implementation strategies while identifying critical bottlenecks that continue to limit widespread adoption.

Similarly, Makhathini *et al.*, emphasized that scale-up challenges remain one of the most significant barriers to commercialization. Economic feasibility depends not only on electrochemical performance but also on capital investment, component durability, maintenance requirements, and integration with existing treatment infrastructure. Recent techno-economic evaluations increasingly suggest that hybrid configurations capable of combining resource recovery with conventional treatment processes may offer the most realistic route toward commercial implementation.

Emerging developments in artificial intelligence, digital twins, advanced materials science, and systems engineering are expected to accelerate MES optimization. Furthermore, integration with renewable energy systems may enable microbial electrochemical technologies to contribute directly to carbon-neutral wastewater treatment and circular economy implementation. As research progresses from proof-of-concept demonstrations toward industrial applications, MESs are increasingly recognized as a key enabling technology for sustainable water, energy, and resource management.

Table 1: Comparative Performance and Energy Metrics of Conventional Wastewater Treatment vs. Microbial Electrochemical Systems

Process Parameter	Conventional Activated Sludge (CAS)	Standalone Microbial Fuel Cells (MFCs)	Hybrid MFC-Membrane Bioreactor (AFMBR)
Primary Objective	Contaminant removal via aeration	Direct electricity generation	High-quality effluent with net-zero energy
Typical Energy Consumption	0.40 to 1.04 kWh per cubic meter	Net energy positive (highly variable)	~0.018 kWh per cubic meter
Aeration Requirement	High (50% to 60% of total energy)	None (Anodic oxidation is anaerobic)	None to minimal
Sludge Yield	High (0.4 to 0.6 kg TSS per kg COD)	Low (0.05 to 0.15 kg TSS per kg COD)	Very low
Peak Power Density	Not applicable	Less than 10 W per square meter	Not applicable
Effluent Quality Limit	Meets strict regulatory discharge	Poor below 150 mg/L COD	High (greater than 92% COD removal)
Scale-up Maturity	Full scale (Global standard)	Pilot scale (Up to 1000 Liters)	Laboratory to early pilot
Capital Cost Drivers	Concrete basins and blower systems	Electrodes and ion-exchange membranes	Biotic separators and membrane module

2. MATERIALS AND METHODS

2.1 Study Design

This study was conducted as a structured narrative and systematic-style literature review focusing on microbial electrochemical systems (MESs) for wastewater treatment and resource recovery. The objective was to critically analyze recent advancements in microbial electrochemical technologies (METs), including microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial desalination cells (MDCs), and microbial electrosynthesis systems.

The review synthesizes experimental, pilot-scale, and modeling studies to evaluate system performance, microbial ecology, electron transfer mechanisms, and techno-economic feasibility. A qualitative evidence synthesis approach was applied to integrate findings across microbiology, environmental engineering, and electrochemical domains.

2.2 Data Sources and Literature Retrieval

Relevant literature was collected from internationally recognized scientific databases to ensure

comprehensive coverage of MES research. The following databases were systematically searched:

- PubMed/MEDLINE
- Scopus
- Web of Science
- ScienceDirect
- SpringerLink
- Google Scholar (for supplementary and citation tracking)

Additional studies were identified through backward and forward citation chaining of key review articles and highly cited experimental papers.

Only peer-reviewed articles published in English were included. Priority was given to publications from 2005–2026, reflecting the rapid development phase of microbial electrochemical technologies.

Search Strategy and Eligibility Criteria

A structured search strategy was developed using combinations of keywords and Boolean operators. The following core terms were used:

- “Microbial electrochemical systems”
- “Microbial fuel cell wastewater treatment”
- “Microbial electrolysis hydrogen production”
- “Extracellular electron transfer mechanisms”
- “Biofilm electrode interaction”
- “Microbial electrosynthesis carbon capture”
- “Wastewater resource recovery circular economy”

Example search string used: (“Microbial electrochemical systems” OR “MFC” OR “MEC”) AND (“wastewater treatment” AND “electron transfer”)

Inclusion Criteria

- Peer-reviewed journal articles, reviews, and meta-analyses
- Studies focusing on MES technologies and wastewater treatment applications
- Experimental, pilot-scale, and modeling-based research
- Articles reporting microbial, electrochemical, or engineering performance data

Exclusion Criteria

- Non-peer-reviewed articles and opinion pieces
- Studies unrelated to wastewater or bioelectrochemical systems
- Purely chemical (non-microbial) electrochemical systems
- Duplicate publications or incomplete datasets

2.3 Microbial Communities and Biofilm Ecology

The overall performance, resilience, and substrate degradation capacity of microbial electrochemical systems (MESS) are heavily dictated by the ecological dynamics and spatial architecture of the

anodic biofilm. While natural domestic wastewater contains highly diverse microbiomes, the selective pressure exerted by a polarized electrode typically enriches specific groups of electrochemically active bacteria (EAB). Consequently, microbial community composition is one of the most critical determinants of electron recovery efficiency, current generation, and long-term reactor stability.

Model Electroactive Microorganisms and Molecular Machinery

The fundamental understanding of extracellular electron transfer (EET) has largely been derived from two extensively studied model organisms, *Geobacter sulfurreducens* and *Shewanella oneidensis* (Logan *et al.*, 2019).

Geobacter species are obligate anaerobes that dominate highly conductive, high-current biofilms. They primarily employ direct electron transfer mechanisms. At the molecular level, this process involves a network of outer-membrane c-type cytochromes, such as OmcZ, which physically interact with the electrode surface. In addition, conductive protein filaments composed largely of OmcS cytochromes function as biological nanowires, enabling cells located several micrometers away from the anode to transfer electrons efficiently. This highly organized electron transport network contributes to the exceptional current densities often observed in *Geobacter*-dominated biofilms.

Shewanella species, in contrast, are facultative anaerobes that utilize a distinct strategy for electron transfer. They employ the metal-reducing (Mtr) pathway, a multi-heme cytochrome complex spanning the cellular envelope, together with soluble redox mediators known as flavins. These endogenous flavins shuttle electrons between microbial cells and the electrode surface, facilitating mediated electron transfer. Although this mechanism allows *Shewanella* to colonize a larger reactor volume, current densities are generally lower than those achieved by *Geobacter*-based systems (Lovley, 2017).

Mixed Microbial Consortia and Syntrophic Networks

Although pure cultures provide valuable mechanistic insights, mixed microbial consortia are essential for practical wastewater treatment applications. Municipal and industrial wastewaters contain complex organic compounds, including proteins, polysaccharides, and lipids, that cannot be directly metabolized by most electroactive bacteria.

As a result, efficient MES operation depends on a structured syntrophic food web involving multiple microbial guilds:

Hydrolysis and Fermentation:

Fermentative microorganisms, including members of the genera *Clostridium* and *Bacteroides*,

degrade complex organic polymers into simpler intermediates, particularly volatile fatty acids (VFAs) such as acetate, propionate, and butyrate

Electro-oxidation:

Electroactive bacteria, particularly members of the family Geobacteraceae, utilize these VFAs as electron donors. During substrate oxidation, electrons are transferred to the anode through extracellular electron transfer pathways.

Interspecies Competition:

Electroactive bacteria compete directly with methanogenic archaea, including Methanosarcina and Methanosaeta, for available substrates and ecological niches. Since methanogens divert electrons toward methane production rather than electrical current generation, excessive methanogenic activity reduces coulombic efficiency. Reactor operators often suppress methanogens by controlling anode potential and operating conditions that favor electroactive bacterial growth.

Recent studies have demonstrated that balanced syntrophic interactions among fermentative bacteria, electroactive bacteria, and methanogenic microorganisms can improve substrate utilization efficiency and overall reactor stability. However, maintaining an optimal microbial community structure remains a major challenge during long-term operation and scale-up.

Biofilm Architecture and Mass Transfer Limitations

The physical structure of electrode-associated biofilms governs the balance between biological activity and mass transfer resistance. Biofilm development generally progresses through four sequential stages:

Initial Attachment:

Planktonic microbial cells approach and reversibly attach to the electrode surface using pili, flagella, and surface adhesion proteins.

Microcolony Formation:

Attached cells proliferate and establish stable microbial aggregates that serve as the foundation for mature biofilm development.

Maturation and Extracellular Polymeric Substance Production:

Microorganisms secrete extracellular polymeric substances (EPS), consisting primarily of polysaccharides, proteins, lipids, and extracellular DNA. The EPS matrix provides structural stability, protects cells from environmental stress, and facilitates electron transport through conductive components embedded within the biofilm.

Detachment and Sloughing: As biofilms continue to grow, nutrient and electron acceptor limitations develop in deeper layers. This can lead to localized cell death and the eventual detachment of biomass from the electrode surface.

The Biofilm Thickness Dilemma

Biofilm thickness exerts a profound influence on electron transfer efficiency and reactor performance. Studies suggest that electroactive biofilms typically perform optimally at thicknesses ranging from approximately 20 to 50 micrometers (μm). Within this range, sufficient microbial biomass is present to generate substantial electrical current while maintaining effective substrate and proton transport.

However, excessively thick biofilms exceeding approximately 100 μm can create severe diffusion limitations. Organic substrates from the bulk liquid are unable to penetrate efficiently into deeper biofilm layers, while metabolically generated protons (H^+) accumulate near the electrode surface. This proton accumulation can significantly reduce local pH values, creating acidic microenvironments that inhibit extracellular electron transfer processes and reduce current generation (Santoro *et al.*, 2017; Kumar *et al.*, 2024).

Conversely, excessively thin biofilms contain insufficient electroactive biomass to support practical current densities. Therefore, maintaining an optimal steady-state biofilm thickness through careful control of hydrodynamic shear forces, substrate loading rates, and reactor operating conditions remains a critical objective in MES engineering and scale-up studies.

Table 2: Major Types of Microbial Electrochemical Technologies

Technology	Main Objective	Energy Input	Main Product
Microbial Fuel Cell (MFC)	Electricity generation	None	Electricity
Microbial Electrolysis Cell (MEC)	Hydrogen production	External voltage	Hydrogen
Microbial Desalination Cell (MDC)	Water desalination	None	Freshwater
Microbial Electrosynthesis System (MES)	CO ₂ conversion	External voltage	Organic chemicals

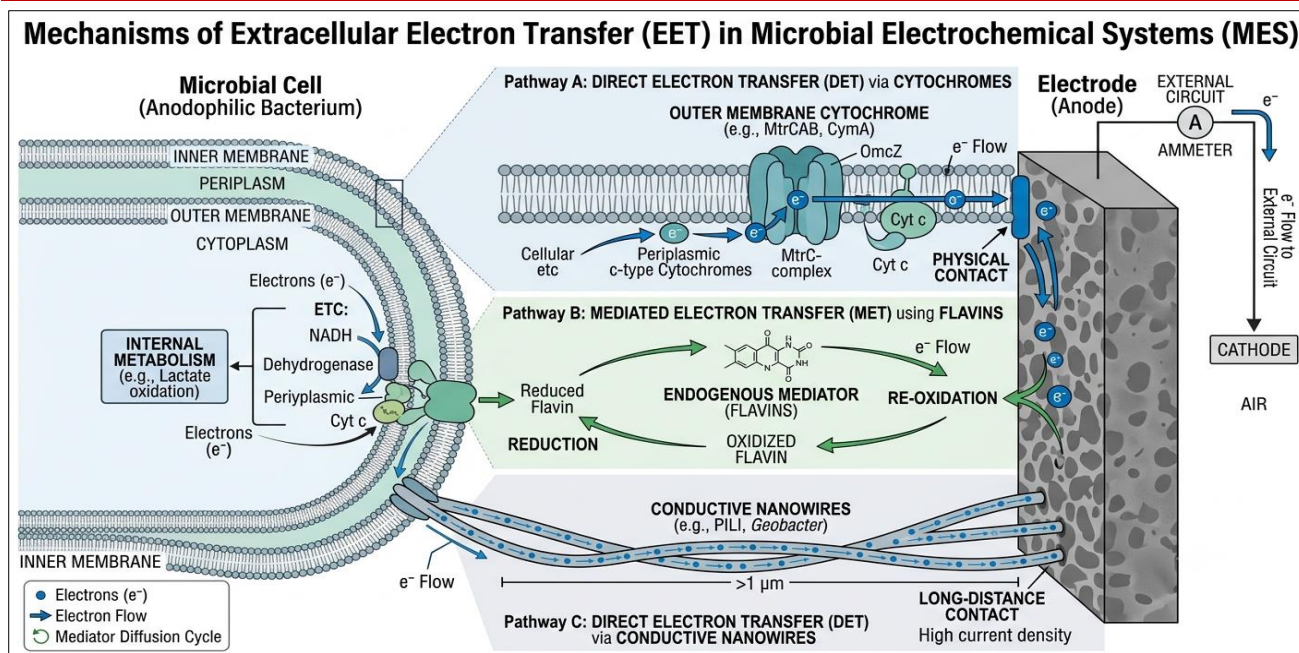


Figure 2: Extracellular Electron Transfer Mechanisms

Figure caption: Major extracellular electron transfer pathways utilized by electroactive microorganisms in microbial electrochemical systems.

Table 3: Representative Electroactive Microorganisms in MESs

Microorganism	Electron Transfer Mechanism	Typical Application
<i>Geobacter sulfurreducens</i>	Direct electron transfer	MFCs, MECs
<i>Shewanella oneidensis</i>	Mediated electron transfer	Bioelectrochemical studies
<i>Pseudomonas aeruginosa</i>	Phenazine-mediated transfer	Mixed-culture reactors
<i>Desulfovibrio vulgaris</i>	Sulfate reduction and EET	Industrial wastewater
Methanogenic archaea	Electromethanogenesis	Methane production

5.3 Carbon Capture and Microbial Electrosynthesis

Recent developments have expanded MES applications beyond wastewater treatment toward carbon capture and utilization. In microbial electrosynthesis systems, electroactive microorganisms utilize electrons supplied by cathodes to reduce carbon dioxide into valuable chemicals such as acetate, ethanol, butyrate, and methane (Nevin *et al.*, 2010; Rabaey & Rozendal, 2010).

A simplified cathodic reaction is represented as:
 $2 \text{CO}_2 + 8 \text{H}^+ + 8 \text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2\text{O}$

Microbial electrosynthesis provides an attractive route for coupling renewable electricity with biological carbon fixation. Integration with solar and wind energy systems may facilitate carbon-neutral production of fuels and commodity chemicals.

Table 4: Resource Recovery Products Generated by MES Technologies

Resource	Recovery Mechanism	Potential Use
Electricity	Anodic oxidation	Power generation
Hydrogen	Cathodic proton reduction	Clean fuel
Methane	Electromethanogenesis	Renewable natural gas
Struvite	Nutrient precipitation	Slow-release fertilizer
Copper	Electrowinning	Metal recovery
Silver	Cathodic reduction	Precious metal recycling
Acetate	Microbial electrosynthesis	Industrial feedstock

6.3 Life Cycle Assessment and Environmental Sustainability

Life Cycle Assessment (LCA) has emerged as an essential tool for evaluating the environmental performance of MES technologies. Recent studies indicate that MESs can reduce greenhouse gas emissions

compared with conventional activated sludge systems by decreasing aeration requirements and enabling resource recovery (Foley *et al.*, 2010; Pant *et al.*, 2012).

However, environmental impacts associated with electrode production, membrane manufacturing,

and reactor construction remain significant. Future sustainability improvements are expected through the development of low-cost carbon-based electrodes, membrane-free reactor configurations, and integration with renewable energy systems.

6.4 Artificial Intelligence and Digital Twins

Artificial intelligence (AI) and machine learning are increasingly being applied to optimize MES operation. Predictive models can estimate power density, current generation, nutrient recovery efficiency, and

microbial community dynamics using operational data collected from reactors.

Digital twin technology represents a particularly promising development. Digital twins create virtual replicas of operating MES reactors, enabling real-time monitoring, predictive maintenance, and process optimization. Recent research suggests that AI-assisted MES management may significantly improve operational stability and scalability while reducing maintenance costs.

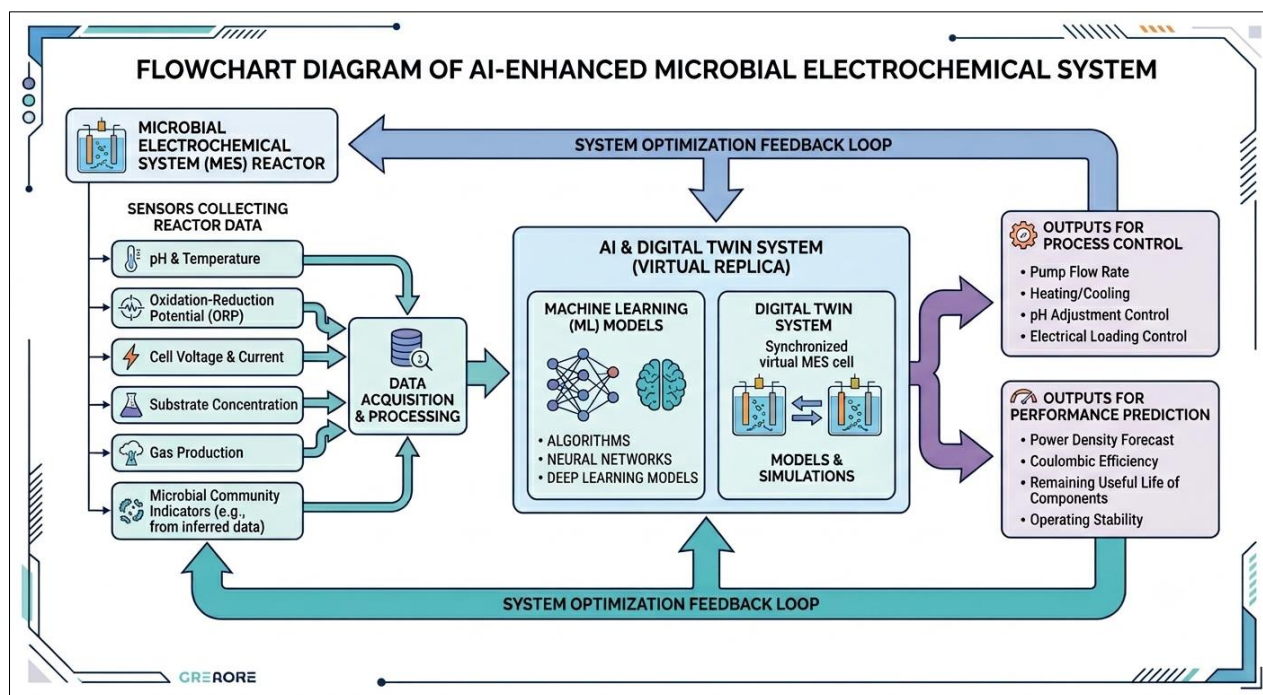


Figure 3: AI-Enhanced MES Operation

7. CONCLUSION AND FUTURE PERSPECTIVES

The transition of wastewater treatment facilities from energy-intensive disposal centers to sustainable, resource-recovering "biorefineries" is an ecological and economic imperative. Microbial Electrochemical Systems (MESs) represent a foundational technological platform capable of driving this shift. By harnessing the unique metabolic capabilities of electrochemically active bacteria, MESs provide a versatile means to extract embedded chemical energy directly as electricity, or to produce high-value chemical commodities like hydrogen gas, methane, and vital agricultural nutrients such as struvite.

This review has demonstrated that while the fundamental principles of extracellular electron transfer are well-understood, and laboratory-scale performance has shown exceptional promise, substantial engineering bottlenecks remain for full-scale implementation. The decrease in power and energy recovery efficiencies upon scaling up driven by internal ohmic resistance, mass-transfer constraints, and membrane biofouling highlights

that standalone MES installations are not yet a viable replacement for conventional activated sludge processes. Moreover, high capital expenditures associated with electrode materials and exchange membranes current limit economic competitiveness.

Therefore, the near-term roadmap for MES implementation lies in process intensification and hybridization. Integrating MES modules into existing treatment trains, such as upstream of membrane bioreactors for bulk COD removal or within anaerobic digesters to accelerate stabilization, offers a pragmatic approach to enhancing WWTP efficiency.

To catalyze the transition from "energy sink to resource mine," future research must prioritize:

Material Innovation: Developing low-cost, durable, 3D electrodes using waste carbon and utilizing terracotta or low-grade textile separators to drastically reduce CAPEX.

Standardized Modular Design: Moving away from bespoke reactor geometries toward standardized,

stackable, "plug-and-play" modules to maintain short ion path lengths while allowing easy capacity scaling.

Real-World Pilot Testing: Long-term operational data using raw, fluctuating wastewater in varied environmental conditions is critical to establishing robust operational protocols and validating techno-economic models.

By addressing these challenges through multi-disciplinary collaboration between microbial ecologists, material scientists, and environmental engineers, MES technology can be moved across the 'valley of death' from pilot scale to industrial implementation. This will facilitate a circular bio-economy where wastewater is no longer viewed as a liability, but as a critical source of clean energy, sustainable water, and valuable resources.

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