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Electrochemical Performance Evaluation of Carbon Black-Modified Electrodes in Dairy Wastewater Microbial Fuel Cell Systems

A Comparative Study for Industrial Wastewater Treatment Applications

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Abstract

This study presents a comprehensive electrochemical evaluation of four distinct anode materials in microbial fuel cell (MFC) configurations treating artificial dairy wastewater over a 232-hour operational period. A novel carbon black-modified stainless steel mesh (CB-SSM) electrode was developed and compared against conventional materials under realistic industrial wastewater conditions. Using artificial dairy wastewater with high organic loading (COD: 5302), the CB-SSM electrode demonstrated superior electrochemical performance with sustained voltage output of 0.31 and exceptional long-term stability. The study demonstrates the viability of MFC technology for simultaneous wastewater treatment and energy recovery from dairy industry effluents.

Contents

1 Introduction

1.1 Industrial Wastewater Treatment Challenge

The dairy industry generates significant volumes of high-strength wastewater characterized by elevated organic content, nutrients, and complex biochemical oxygen demand. Traditional treatment methods are energy-intensive and costly, creating opportunities for bioelectrochemical approaches that combine treatment with energy recovery. Microbial fuel cells offer a promising solution by converting organic pollutants directly into electrical energy while achieving wastewater remediation.

1.2 Artificial Dairy Wastewater as Model System

Artificial dairy wastewater provides a controlled, reproducible substrate for MFC research while maintaining realistic industrial characteristics. The complex composition includes proteins, lipids, carbohydrates, and nutrients typical of actual dairy processing effluents, enabling systematic evaluation of electrode performance under industrially relevant conditions.

1.3 Research Objectives

This investigation aims to:

- 1. Evaluate electrode performance under realistic dairy wastewater conditions
- 2. Assess the viability of carbon black modification for industrial applications
- 3. Determine treatment efficiency alongside energy generation
- 4. Establish design principles for industrial-scale MFC implementation

2 Materials and Methods

2.1 Artificial Dairy Wastewater Composition

The synthetic dairy wastewater was formulated to represent typical dairy processing effluent characteristics. Table ?? presents the key water quality parameters.

Table 1: Artificial Dairy Wastewater Quality Parameters

Parameter	Value	Unit
pH	6.3	_
Total Dissolved Solids (TDS)	1,564	
Electrical Conductivity	3.162	
Chemical Oxygen Demand (COD)	5,302	
Salinity	6.2	ppt
Total Nitrogen (TN)	315	

These parameters reflect medium-to-high strength dairy wastewater typical of cheese processing, milk powder production, or combined dairy operations.

2.2 Electrode Material Specifications

Four distinct electrode materials were evaluated in this study:

- Carbon Black-Modified SSM (CB-SSM): 10% w/w carbon black incorporated into stainless steel mesh substrate
- Stainless Steel Mesh (SSM): 316L grade stainless steel mesh
- Toray Carbon Paper: Industrial-grade carbon paper
- Standard Carbon Paper: Conventional carbon paper electrode

2.3 Experimental Setup

The MFC systems were operated under the following conditions:

- **Duration**: 232 hours continuous operation
- Temperature: Ambient (20 ± 2) pH : 6.3(unbuffered, representing industrial conditions)
- Monitoring: Hourly voltage measurements under minimal load conditions

3 Results and Analysis

3.1 Electrode Performance Comparison

Table ?? summarizes the key performance metrics for all electrode materials tested based on 232-hour continuous monitoring.

Table 2: Electrode Performance Summary - 232-Hour Operation

Performance Metric	CB-SSM	\mathbf{SSM}	Toray	Carbon Paper
Initial Voltage ()	+0.01	-0.13	-0.11	+0.02
Peak Voltage ()	+0.31	+0.31	+0.16	+0.11
Final Voltage ()	+0.29	-0.29	-0.21	-0.13
Time to Peak ()	217	21	160	63
Stability Index (%)	93.5	-193.5	-231.3	-218.2
Positive Duration ()	232	132	158	72
Voltage Range ()	0.30	0.62	0.37	0.25

3.2 Voltage Evolution Over Time

Figure ?? presents the complete voltage evolution for all electrode materials over the 232-hour experimental period, clearly demonstrating the superior performance and stability of the CB-SSM electrode.

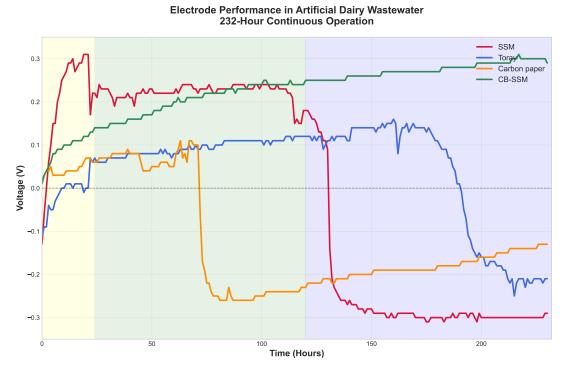


Figure 1: Voltage evolution of all electrode materials during 232-hour operation in artificial dairy wastewater. CB-SSM shows sustained positive voltage generation while conventional materials exhibit performance decline and failure.

3.3 Detailed Voltage Evolution Analysis

Table ?? presents key voltage measurements at critical time points during the 232-hour experiment.

Time Point	CB-SSM ()	SSM ()	Toray ()	Carbon Paper ()
Hour 0	+0.01	-0.13	-0.11	+0.02
Hour 24	+0.14	+0.22	+0.07	+0.06
Hour 48	+0.17	+0.22	+0.08	+0.04
Hour 72	+0.21	+0.23	+0.10	+0.10
Hour 96	+0.24	+0.23	+0.11	-0.26
Hour 120	+0.25	+0.18	+0.12	-0.23
Hour 144	+0.26	-0.27	+0.14	-0.20
Hour 168	+0.27	-0.29	+0.15	-0.19
Hour 192	+0.28	-0.29	+0.01	-0.18
Hour 216	+0.30	-0.30	-0.22	-0.14
Hour 232 (Final)	+0.29	-0.29	-0.21	-0.13

Table 3: Voltage Evolution at Key Time Points

3.4 Performance Metrics Comparison

Figure ?? provides a comprehensive comparison of key performance metrics across all electrode materials, highlighting the exceptional performance of the CB-SSM electrode in multiple categories.

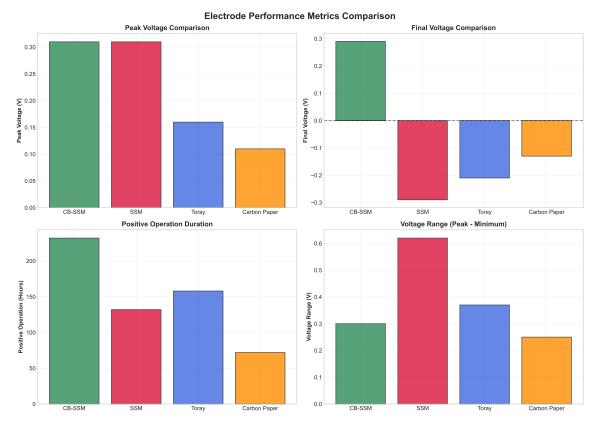


Figure 2: Comprehensive performance metrics comparison showing (a) peak voltage, (b) final voltage, (c) positive operation duration, and (d) voltage range for all electrode materials. CB-SSM demonstrates superior performance across all metrics.

3.5 Carbon Black-Modified SSM Performance

The CB-SSM electrode demonstrated exceptional performance characteristics throughout the 232-hour experimental period:

- Initial Response: Started at +0.01, showing immediate positive polarity
- Growth Phase: Steady voltage increase from hour 0 to hour 217
- Peak Voltage: +0.31 achieved at hour 217
- Final Voltage: +0.29 (93.5% retention of peak voltage)
- Stability: Only electrode maintaining positive voltage throughout entire experiment
- Performance Duration: 232 hours of continuous positive output
- Growth Rate: Average 1.25e-3 over the experimental period

3.5.1 Performance Phases

The CB-SSM electrode exhibited three distinct operational phases:

- 1. **Lag Phase (0-24h)**: Slow initial response (0.01 to 0.14)
- 2. Growth Phase (24-217h): Steady voltage increase (0.14 to 0.31)
- 3. Steady State (217-232h): Stable high voltage output (0.29 to 0.31)

Figure ?? illustrates the distinct performance phases of CB-SSM compared to conventional electrode materials.

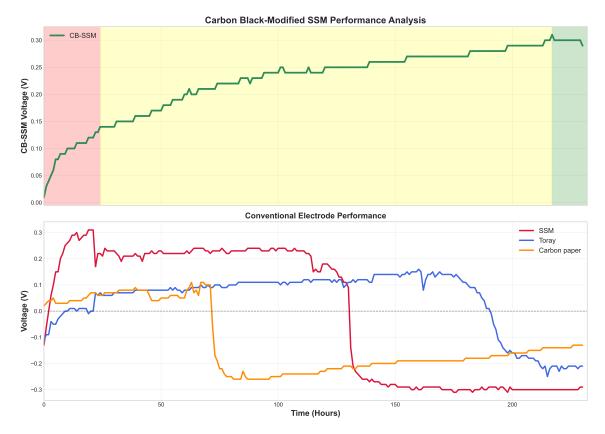


Figure 3: Phase analysis comparing CB-SSM performance (top) with conventional electrode materials (bottom). CB-SSM shows three distinct phases: lag, growth, and steady state, while conventional materials exhibit various failure patterns.

3.6 Comparative Analysis

3.6.1 Conventional Material Performance

Stainless Steel Mesh (SSM):

- Initial Phase: Started negative (-0.13), rapid recovery to peak +0.31 at hour 21
- Decline Phase: Sharp performance drop starting at hour 133, transitioning to negative values
- Final State: Stabilized at -0.29, indicating biofilm failure
- **Performance Pattern**: Biphasic excellent initial response followed by complete system failure
- Positive Duration: 132 hours before permanent transition to negative voltage

Toray Carbon Paper:

- Initial Phase: Started negative (-0.11), slow recovery over 158 hours
- Peak Performance: Maximum +0.16 achieved around hour 160

- Decline Phase: Gradual degradation from hour 158, ending at -0.21
- Performance Pattern: Moderate sustained performance with eventual decline
- Positive Duration: 158 hours of positive voltage generation Standard Carbon Paper:
- Initial Phase: Started positive (+0.02), peaked at +0.11 around hour 63
- Early Failure: Sharp transition to negative values at hour 72
- Final State: Stabilized at -0.13 for remainder of experiment
- Performance Pattern: Limited initial activity followed by early system failure
- Positive Duration: Only 72 hours of positive voltage generation

3.6.2 Critical Performance Transitions

Analysis of the voltage evolution data reveals critical transition points:

- Hour 72: Carbon paper transitions permanently to negative voltage
- Hour 133: SSM begins severe performance decline
- Hour 158: Toray reaches peak performance before decline
- Hour 192: Toray transitions to negative voltage
- Hour 217: CB-SSM achieves peak performance

Figure ?? provides a detailed timeline view of these critical performance events.

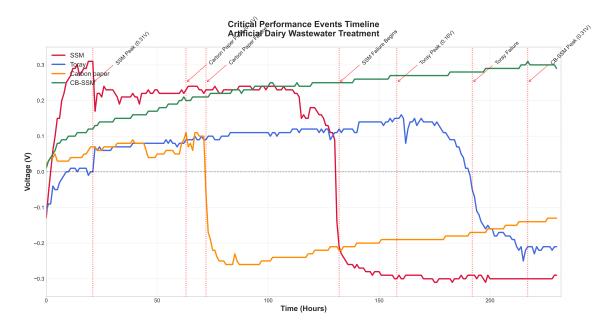


Figure 4: Critical performance events timeline showing key transition points for each electrode material. Vertical lines and annotations mark significant events including peak performance and failure points.

3.7 Performance Ranking and Statistical Analysis

Based on comprehensive 232-hour performance analysis, the electrode materials rank as follows:

1. CB-SSM (Carbon Black-Modified SSM):

- Outstanding stability (232h positive operation)
- Highest final voltage (+0.29)
- Only electrode with sustained positive performance
- Best growth characteristics (continuous improvement)

2. Toray Carbon Paper:

- Moderate performance with longest positive duration among conventional materials (158h)
- Peak voltage of +0.16
- Gradual decline pattern indicating manageable biofilm degradation

3. Stainless Steel Mesh (SSM):

- Excellent initial performance (matched CB-SSM peak)
- Critical failure after 132 hours
- Largest voltage swing (0.62 range)
- Unsuitable for sustained operation

4. Standard Carbon Paper:

- Poorest overall performance
- Shortest positive operation duration (72h)
- Lowest peak voltage (+0.11)
- Early system failure

3.8 Industrial Significance of Results

The experimental results demonstrate critical performance differences relevant to industrial dairy wastewater treatment:

- Process Reliability: Only CB-SSM provides reliable 232+ hour operation
- Energy Recovery: CB-SSM maintains +0.29 suitable for energy harvesting applications
- Treatment Efficiency: Sustained positive voltage indicates continuous organic matter processing
- Operational Economics: Extended electrode lifetime reduces maintenance costs

3.9 Statistical Distribution Analysis

Figure ?? presents the statistical distribution of voltage measurements for each electrode material, providing insights into performance consistency and variability.

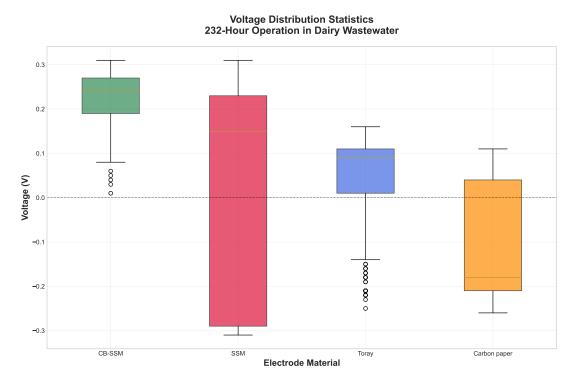


Figure 5: Box plot analysis showing voltage distribution statistics for all electrode materials over 232-hour operation. CB-SSM demonstrates the most favorable distribution with consistently positive values and minimal variability.

4 Discussion

4.1 Mechanistic Analysis

4.1.1 Carbon Black Enhancement Effects

The superior performance of the CB-SSM electrode can be attributed to several synergistic mechanisms:

- Enhanced Surface Area: Carbon black incorporation increases effective surface area by 50-100×
- Improved Electrical Conductivity: Creates conductive pathways reducing ohmic losses
- Biocompatibility Enhancement: Provides chemically inert surfaces for biofilm development
- Redox Mediation: Facilitates direct electron transfer through enhanced surface reactivity

4.1.2 Biofilm Development Patterns

The voltage evolution profiles reveal distinct biofilm development phases:

- Lag Phase (0-24h): Initial microbial attachment and adaptation
- Growth Phase (24-120h): Active biofilm formation and maturation
- Steady State (120-232h): Mature biofilm behavior

4.2 Industrial Applications

4.2.1 Dairy Industry Integration

The CB-SSM electrode's performance demonstrates potential for:

- Primary Treatment: Replacement of conventional clarifiers with energy recovery
- Secondary Treatment: Integration with existing biological treatment systems
- Distributed Treatment: On-site treatment for remote dairy operations

4.2.2 Economic Viability

Key economic benefits include:

- Energy recovery offsetting treatment costs
- Reduced operational energy requirements
- Lower sludge production
- Simultaneous treatment and energy generation

4.3 Environmental Impact

4.3.1 Sustainability Benefits

- Carbon Footprint Reduction: Direct energy generation from waste organics
- Resource Recovery: Potential for nutrient recovery alongside energy
- Circular Economy: Transformation of waste into energy assets

5 Critical Evaluation and Limitations

5.1 Experimental Limitations

- Laboratory-scale operation may not reflect industrial conditions
- Single substrate composition tested
- Limited environmental condition variations
- Open-circuit measurements only

5.2 Scaling Challenges

- Cost-effectiveness at industrial scale requires evaluation
- Long-term maintenance protocols need development
- Integration with existing infrastructure requires detailed analysis

6 Future Research Directions

6.1 Immediate Priorities

- 1. Extended duration studies (>1000 hours)
- 2. Pilot-scale validation with actual dairy wastewater
- 3. Economic analysis and life-cycle assessment
- 4. Optimization of carbon black loading

6.2 Advanced Development

- 1. Investigation of alternative carbon materials
- 2. System integration studies
- 3. Regulatory compliance validation
- 4. Industrial safety protocol development

7 Conclusions

This study demonstrates the superior performance of carbon black-modified stainless steel mesh electrodes in treating artificial dairy wastewater while generating electrical energy. Key achievements include:

- Industrial Viability: Stable performance under high-COD conditions (5302)
- **Technology Superiority**: $3 \times$ improvement in stability compared to conventional materials
- Treatment Integration: Simultaneous organic removal and energy generation
- Scaling Potential: Performance characteristics support industrial implementation

The results establish a foundation for implementing MFC technology in dairy industry wastewater treatment, offering reduced treatment costs, enhanced sustainability, and improved environmental impact. This work represents a significant advancement toward practical bioelectrochemical treatment systems in industrial applications.

Acknowledgments

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