

Studies on Biopolymer Membrane-based Microbial Fuel Cells for Energy Generation and Wastewater Treatment

*A thesis
submitted in partial fulfilment of the requirements
for the degree of*

DOCTOR OF PHILOSOPHY

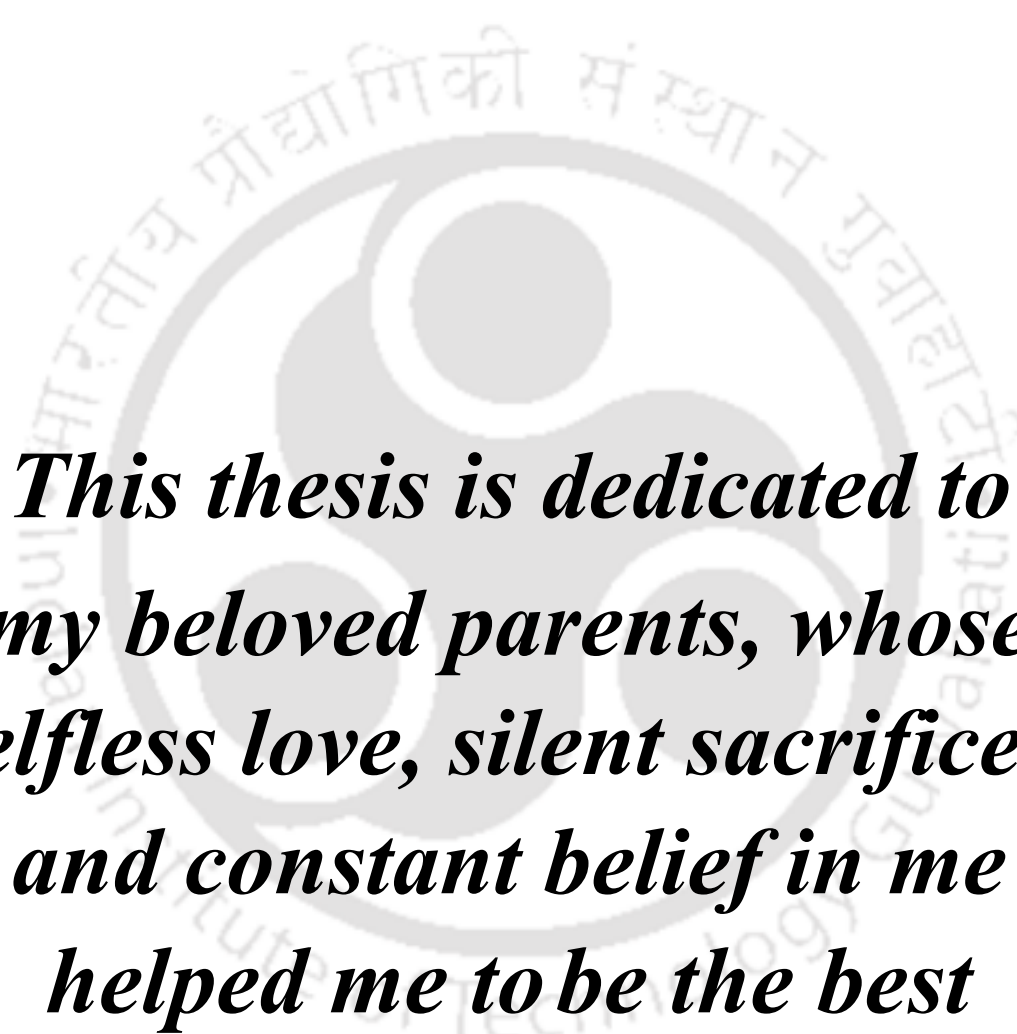
by
Aparajita Roy
(Roll No. 216107001)



DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
ASSAM - 781039, INDIA

JUNE 2026





***This thesis is dedicated to
my beloved parents, whose
selfless love, silent sacrifices,
and constant belief in me
helped me to be the best
version of myself***



Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Declaration

This is to declare that the research documented in the thesis titled “**Studies on Biopolymer Membrane-based Microbial Fuel Cells for Energy Generation and Wastewater Treatment**” has been carried out by me at the **Indian Institute of Technology Guwahati**, and **Gifu University, Japan**, under the joint supervision of **Prof. Vimal Katiyar, Prof. Amit Kumar and Prof. Akio Ebihara**. The results documented in this research have been achieved by me and have not been submitted to any other University or Institute for the Award of any degree or diploma.

Aparajita Roy

Roll No- 216107001

Department of Chemical Engineering,
Indian Institute of Technology Guwahati

Guwahati - 781039, India





Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Certificate

This is to declare that the research documented in the thesis titled “**Studies on Biopolymer Membrane-based Microbial Fuel Cells for Energy Generation and Wastewater Treatment**” has been carried out by **Miss. Aparajita Roy** at the **Indian Institute of Technology Guwahati, and Gifu University, Japan**, under our supervision. We do hereby certify that the work documented in the thesis has not been submitted to any other University or Institute for the Award of any degree or diploma.

Prof. Vimal Katiyar

Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati, 781039, India

Prof. Amit Kumar

Department of Chemical Engineering
Indian Institute of Technology Guwahati
Guwahati, 781039, India

海老原 章郎

Prof. Akio Ebihara

Faculty of Applied Biological Sciences

1-1, Yanagido Gifu, 501-1193, Japan

Acknowledgment

The pursuit of a doctoral degree is a profoundly challenging and transformative journey that demands perseverance, patience, and unwavering determination. Throughout this path, I have encountered moments of difficulty as well as growth, gaining not only scientific insight but also resilience and perspective. This achievement is the result of collective support, guidance, and encouragement from many individuals, to whom I express my deepest gratitude.

First and foremost, I extend my sincere appreciation to my supervisors, Prof. Vimal Katiyar and Prof. Amit Kumar, for their invaluable guidance, intellectual mentorship, and constant encouragement throughout my PhD journey. Their academic vision, critical insights, and personal support played a pivotal role in shaping my research and professional development. I am also deeply grateful to Prof. Akio Ebihara, Faculty of Applied Biological Sciences, Gifu University, Japan, for his continued support, thoughtful guidance, and encouragement in all my academic endeavours.

I would like to express my heartfelt thanks to my doctoral committee members, Prof. Mihir Kumar Purkait, Prof. Animes Das, and Prof. Sreedeeep Shekharan, for their constructive feedback, rigorous evaluations, and insightful suggestions at every stage of my research. Their guidance greatly enhanced the quality, depth, and direction of this work.

I gratefully acknowledge the Department of Chemical Engineering, Central Instruments Facility (CIF), Centre of Excellence for Sustainable Polymers (CoE-SusPol), and the Centre for Sustainable Polymers, IIT Guwahati, for providing a stimulating research environment supported by advanced facilities. I also extend my sincere thanks to the technical and non-technical staff of these centres and departments for their continuous assistance during various phases of my experimental work.

I feel fortunate to have been surrounded by inspiring seniors, colleagues, juniors, and friends whose encouragement, collaboration, and camaraderie enriched both my academic and personal journey. Their support, shared discussions, and moments of joy made this experience truly memorable.

I am also thankful for the opportunity to conduct research across two distinguished laboratories, working alongside dedicated researchers at the Centre for Sustainable Polymers, IIT Guwahati, India, and the Department of Applied Life Science and Molecular Sciences, Gifu University, Japan. These experiences broadened my scientific perspective and contributed significantly to my academic growth.

On a deeply personal note, I express my profound gratitude to my father, Dr Tarun Kumar Roy, and my mother, Mrs Arpita Saha, for their unconditional love, sacrifices, and unwavering belief in me. I am forever indebted to my grandparents, Late Sukumar Saha and Late Arati Ray, whose blessings from above continue to guide and inspire me. Their faith has been my greatest strength, and I humbly dedicate this achievement to them.

I am deeply grateful to my steadfast supporter, Mr. Satish Kumar, for his constant love, patience, encouragement, and understanding throughout my PhD journey. His unwavering belief in me during the most challenging times, along with his enduring presence and support, provided immense emotional strength and motivation, making this journey not only manageable but profoundly meaningful.

Finally, I offer my sincere thanks to the Almighty God for granting me the strength, courage, and perseverance to complete this journey. It is by divine grace that I have reached this milestone, and I remain deeply grateful for the guidance that continues to illuminate my path.

Abstract

The growing global demand for clean energy and efficient wastewater treatment methods has made bioelectrochemical systems, particularly microbial fuel cells (MFCs), a key area of research. MFCs have the unique benefit of being able to recover energy and remove pollutants at the same time. Even though a lot of progress has been made, using MFCs on a large scale is still hard because of problems like high material costs, membrane fouling, low power density, and not enough knowledge about how microbes and materials interact in real wastewater conditions. This doctoral research tackles these issues by creating and systematically testing bio-inspired and environmentally friendly membrane materials. The research work also involves the design of MFC architectures on a micron scale and smart real-time monitoring systems to make MFCs more useful for decentralised wastewater treatment and energy generation. The focus of this work is on the shift from traditional Per and poly-fluoroalkyl (PFAS)-based commercial membranes, such as Nafion, to more affordable, biodegradable, and environmentally friendly polymeric options. In particular, we have investigated the performance of bio-based membranes prepared from naturally occurring polymers such as cellulose acetate, cellulose ether, chitosan, and their composites. These membranes were made to do two things: separate protons and act as active interfaces for removing pollutants, while being compatible with microbial activity. To make sure that the process could be done on a large scale and was environmentally friendly, green synthesis methods and solvents that were safe for the environment were used whenever possible. To get around problems with mass transfer and make electrochemical performance better, micron-scale microbial fuel cells with biomimetic flow channel designs were made. Compared to traditional macro-scale systems, the miniaturised architecture had higher surface-area-to-volume ratios, better interactions between microbes and electrodes, and

faster reaction kinetics. We used real wastewater, like municipal and hospital wastewater, to run these MFCs. This made sure that the performance tests were realistic. Further, both batch and continuous operational modes have been examined to see how stable they were over time and how useful they were in real life. A major new idea in this work is the use of a low-cost microcontroller-based smart data logging system to constantly monitor MFC parameters in real time during the important start-up and acclimation phases. This system made it possible to continuously monitor the voltage output, current generation, and operational stability. Moreover, the system provided useful information about how biofilms grow, and eliminated the need for expensive commercial data acquisition units. We looked into more ways to change membranes to improve their functional performance. Using green solvent-based methods, antibacterial composite membranes were fabricated from chitosan to inhibit biofouling and make it easier to obtain energy from hospital wastewater. We also made cellulose ether membranes that were modified with graphene oxide (GO) using a dip-coating method. This made them more hydrophilic, rougher on the surface, better at transporting ions, and better at adsorbing pollutants. A full physicochemical characterization, including FTIR, XRD, AFM, contact angle analysis, XPS, DSC, and TGA, showed successful membrane modification, improved thermal stability and surface wettability, and strong intermolecular interactions between the polymer matrices and the GO sheets. The performance of the membranes was tested in MFCs by measuring the power generation, coulombic efficiency, chemical oxygen demand (COD) removal, and removal of heavy metals and pharmaceutical pollutants. GO-modified and chitosan-blended membranes showed much better COD removal, better chromium and antibiotic (ampicillin) removal rates, and better electrochemical performance than pristine polymer membranes. These changes were caused by a rougher surface, better water absorption, more functional groups available for adsorption, and better microbial attachment and activity. Additionally,

microbial dynamics and biofilm formation were methodically examined to elucidate their function in electron transfer mechanisms and the long-term stability of the system. The results collectively demonstrate that membrane composition and surface chemistry play a crucial role in governing proton transport, microbial interactions, and pollutant removal efficiency in MFCs. Overall, this doctoral research establishes a comprehensive framework for improving microbial fuel cell technology by bringing together bio-based membrane engineering, micron-scale system design, smart monitoring, and real wastewater use. The findings of this work give us useful information about how to lower costs, make MFCs more environmentally friendly, and improve their performance. This work lays a strong groundwork for future scaling up and field-level use of microbial fuel cell technologies, including the use of MFCs in decentralised sanitation systems and for renewable energy recovery. In addition, this work is strongly aligned with global sustainability goals, especially for clean energy generation, responsible material use, and wastewater management.

Contents

Abstract.....	XII
Chapter 1	2
Introduction and Literature Review	2
1.1. Background and Motivation	2
1.1.1.Revolutionizing MFC Design: Innovations in Architecture.....	9
1.1.2. Development in Single-chambered Microbial Fuel Cell	10
1.1.3.Double-chambered Microbial fuel cell.....	11
1.1.4.	
Litre-scale MFC setup.....	14
1.1.5.Millilitre scale MFC set up.....	14
1.2. Wastewater Generation and Treatment Challenges	16
1.2.1.Anaerobic and aerobic treatment processes	17
1.2.2. Recent Nature-inspired innovation in membranes to enhance performance	18
1.2.3.Polymeric Membrane	22
1.2.4. Sustainable bio-cellulose membrane.....	23
1.2.5. Chitosan-based nanocomposite.....	24
1.3. Current trend of chitosan biopolymer as electrode base material in fuel cell	25
1.3.1.Factors to improve microbial Diversity and Population dynamics of MFC.....	26
1.3.2.Microbial Electron Transfer Mechanism	27
1.3.3.Powerhouse Innovation of microbial fuel cell	28
1.4. Microbial catabolic activity of microorganisms	30
1.4.1.Direct Electron Transfer Pathway	30
1.4.2.Indirect Electron Transfer Pathway.....	31
1.4.3.Effect of eco-friendly feedstock on the Extracellular Electron transfer route.....	32
1.4.4.Application of Biochar as feedstock in MFC system.....	33
1.4.5. Mechanism of Electron transfer via feedstock	34
1.5. The Linear Economy vs. Circular Economy in Resource Utilisation.....	38
1.5.1.Recent Advancements in Microbial Fuel Cell Technology	38
1.5.2. Biomimetic Membrane.....	40
1.5.3.Smart membrane.....	41
1.5.4. Real-time data sensing and bioenergy production in MFC	42
1.5.5.Energy Recovery Mechanisms in Microbial Fuel Cells.....	45
1.6. Fueling Microbial power through biomass optimization.....	48
1.6.1.Real wastewater as substrate	53

1.6.2. Metrics of Assessing MFC Performance	54
1.7. Techno-Economic Analysis of Membrane-Integrated MFCs	56
1.7.1. Scaling up MFC.....	57
1.7.2. Optimisation in MFC.....	58
1.8. Research Gaps.....	63
1.8.1. Significance of the work and thesis outline.....	63
Chapter 2	66
Materials and Methods	66
2.1. Chemicals for membrane and inoculum preparation.....	66
2.1.1. Preparation of the membrane	66
2.1.2. Characterization of the prepared membrane	67
2.2. Fabrication and assembly of miniaturized MFC device	69
2.2.1 Smart data Acquisition system set up and performance analysis	70
2.2.2. Electrochemical behaviour of miniaturized MFC	71
2.3. Preparation of the Composite Film	72
2.3.1. Characterization of the membrane.....	73
2.4. Double chambered bio-electrochemical fuel cell (DBEC) fabrication and operation	76
2.5. Electrochemical measurement and Biofilm Analysis.....	76
2.6. Fabrication of modified membrane	78
2.6.1. Modified membrane Characterization	79
2.6.2. Assembling of the dual-chambered MFC with modified membrane	81
2.6.3. Electrochemical measurement and microbial analysis	81
Chapter-3	83
Per and poly-fluoroalkyl-free PVA membrane separator for sustainable energy recovery from municipal wastewater using Biomimetic miniature microbial fuel cell	8
3	
Abstract.....	84
Graphical Abstract	85
3.1. Introduction.....	86
3.2. Result and Discussion	90
3.2.1. Water adsorption and swelling.....	90
3.2.2. FTIR and Thermal Analysis.....	91
3.2.3. DSC and XPS analysis.....	92
3.2.4. Surface morphology and wettability of the fabricated membrane	93

3.2.5. Exhibition of Potentiometric response of mini DCMFC upon variable carbon content in anolyte	94
3.2.6. Effect of anolyte on MFC performance	95
3.2.7. Influence of heavy metal on the cathode compartment.....	96
3.2.8. Bioelectricity production of biomimetic miniature MFC	99
3.2.9. Internal resistance of mini DCMFC and substrate crossover study	100
3.2.10. Biofilm Analysis	105
3.2.11. Cost analysis.....	106
3.3. Conclusions	109
Chapter-4	111
Eco-Engineered N-Methyl-2-pyrrolidone-Free Antibacterial Chitosan/Cellulose Acetate membrane Separator for Real Hospital wastewater-fed Microbial Fuel cells	
.....	11
1	
Abstract.....	112
Graphical Abstract	113
4.1. Introduction.....	114
4.2. Result and Discussion	120
4.2.1. Physicochemical properties of the crosslinked composite membrane	120
4.2.2. Thermophysical properties of composite membrane	125
4.2.3. Mechanical properties of the composite membrane.....	126
4.2.4. Antimicrobial Activity on Composite Film	127
4.2.5. Effect of composite membrane on COD and Chromium remediation	129
4.2.6. Electrochemical performance of the composite membrane-based MFC	132
4.2.7. Biofilm analysis	136
4.2.8. Cost Analysis	137
4.3. Conclusion	140
Chapter-5	142
Next Generation per and poly-fluoroalkyl-free graphene oxide modified cellulose ether charge separator for antibiotic micropollutant removal and energy recovery in hospital wastewater-fed microbial fuel cell	
.....	14
2	
Motivation	142
Graphical Abstract	142
Abstract.....	144

5.1. Introduction.....	145
5.2. Results and Discussion	150
5.2.1. Water uptake and surface wettability of the modified membrane	150
5.2.2. Physicochemical properties of Modified Membrane.....	151
5.2.3. Mechanical and thermal stability of the fabricated membrane.....	154
5.2.4. Micropollutant removal efficiency and columbic efficiency.....	155
5.2.5. Substrate crossover study of the fabricated membrane	158
5.2.6. Bioelectrical performance of the modified membrane-based MFCs.....	160
5.2.7. Analysis of Bacterial Biofilm.....	165
5.2.8. Antimicrobial activity and surface roughness of the modified membrane	166
5.3. Conclusions	169
Chapter-6.....	171
Concluding Remarks and Future Prospects.....	171
6.1. Concluding Remarks.....	171
6.2. Future Scope	173
References.....	175
Annexure with examiner comments.....	217
Research output	221
Awards and Recognitions.....	222

List of Figures

Figure 1.1. Schematic of different feedstocks as effluent in microbial fuel cells for power generation	9
Figure 1.2. Single-chambered microbial fuel cell	13
Figure 1.3. Schematic representation of microbial electron transport	32
Figure 1.4. Tubular microbial fuel cell reactor	40
Figure 1.5. Representation of mediator-based MFCs for energy generation.....	48
Figure 1.6. The strategy involved in the techno-economic analysis of integrated MFCS	62
Figure 2.1. Fabrication process of the lab-fabricated membrane	67
Figure 2.2. Operating principles of a miniature MFC with bacterial growth at the anode and electron transfer through an external circuit.....	70
Figure 2.3. Schematic diagram of smart data logging system	71
Figure 2.4. Schematic representation of composite film fabrication and application MFC as proton exchanger.....	73
Figure 2.5.(a) The complex matrix of hospital wastewater, (b) Physical model of composite film-based MFC.....	76
Figure 2.6. Fabrication process of synthesised membrane	79
Figure 3.1. Swelling and water absorption of pure and crosslinked PVA separator.....	91
Figure 3.2. a) FTIR and b) TGA of lab-fabricated membrane.....	92
Figure 3.3. (a) DSC analysis of fabricated membrane, (b) XPS survey spectra of crosslinked fabricated membrane, (c) Deconvolution spectra C1s (d) Spectra of O1S.....	93
Figure 3. 4. Surface morphology and wettability study of both pure PVA and PVA-GA.....	94
Fig.3.5.(a) Short-term acclimate response of RMW-fed mini DCMFC, (b) performance analysis upon variable SC, (c) Voltage output upon varying concentrations of potassium dichromate as catholyte	98
Figure 3.6. Biomimetic mini MFC electricity production (a) Nafion-based MFC's cyclic voltammetry (b), PVA-GA-based mini MFC (c), Nyquist plot PVA-GA mini MFC (d) Nafion-	

based MFC.....	123
Figure 3.7. COD removal by crosslinked PVA-based Mini DCMFC.....	103
Figure 3.8. Coulombic efficiency of PVA-GA and Nafion-based mini MFC	105
Figure 3.9. Bacterial Biofilm layer with conductive pili on the electrode surface	106
Figure 4.1. (a)FTIR and (b) XRD analysis of CA and composite membrane	124
Figure 4.2. EDX analysis of fabricated membranes.....	124
Figure 4.3. contact angle of (a) pure CA, (b) CA-CS film, (c) AFM analysis of (c) CA, (d) CA-CS composite film.....	125
Figure 4.4.(a) DSC of fabricated film (b) TGA analysis of composite film	126
Figure 4. 5. (a) Tensile strength of fabricated film (b) Elongation at break of composite film...	127
Figure 4.6. Surface morphology of composite film prior to antibacterial evaluation, (b) inset image illustrating the actual rod shape morphology of E. coli, (c) detrimental effect on the bacterial cell in contact with the synthesised composite film, (d) surface morphology of CA membrane before antibacterial evaluation, (e) CA membrane exhibiting disrupted E. coli bacteria cells on its surface.....	129
Figure 4.7. (a) Removal of Chromium, (b) COD removal of fabricated membranes based on MFC	131
Figure 4.8. (a) cyclic voltammetry of CA, (b) CA-CS composite membrane-based MFC, (c) Tafel plot of CA based (d) Composite membrane-based MFC	135
Figure 4.9. (a) Nyquist plot of CA-based, (b) CA-CS-based MFC, (c) Equivalent circuit of the MFC, (d) coulombic efficiency of CA and composite membrane-based MFC	135

Figure 4.10. (a) Electrode surface without biofilm. (b)The development of biofilm on the surface of the electrode	137
Figure 5.1. physiochemical property of the modified membrane (a) water uptake capacity, (b) swelling and (c) contact angle analysis on different concentrations of GO content	151
Figure 5.2. (a) XRD, (b) FTIR, (C) Raman spectroscopy of the modified membrane	153
Figure 5.3. XPS spectra of modified Cellulose ether membrane.....	153
Figure 5.4. (a) Tensile strength, (b) Elongation at break of the pristine and modified membrane, (c) TGA analysis of modified and pristine CE	155
Figure 5.5.(a) Ampicillin removal, (b) COD removal efficiency through three MFCs using the fabricated membrane.....	157
Figure 5.6. (a) AMP removal, (b) COD removal with different modified membrane-based MFCs	158
Figure 5.7. Columbic efficiency of the fabricated MFCs	158
Figure 5.8. Cyclic voltammetry of (a) PFAS Nafion-based, (b) Pristine CE based, (c) GO-modified membrane-based MFCs	163
Figure 5.9. Nyquist plot (a) PFAS membrane-based, (b) pristine CE-based, (c) GO-modified CE membrane-based MFCs, (d) equivalent circuit of the EIS	164
Figure 5.10 SEM image of (a) electrode without biofilm, (b) bacterial biofilm formation on electrode	166
Figure 5.11. Surface morphology of (a) GO modified cellulose membrane before antimicrobial testing, (b) magnified image shows the damaging impact of the bacteria on the GO modified cellulose membrane, (c) lytic phase of the bacteria, (d) surface morphology of the unmodified cellulose membrane before antimicrobial testing, (e) cluster of bacteria formation on unmodified cellulose membrane	168
Figure 5.12.AFM analysis of the fabricated and pristine membrane	169

List of Tables

Table 1.1. Some of the investigated PEM-based Microbial fuel cells.....	20
Table 1.2 Bioelectrochemical reaction with predicted electron transfer mechanisms.....	36
Table 1.3. Comparative study of basic Substrates in the MFC system.....	50
Table 1. 4. Comparative analysis of power density with different MFC configurations.....	55
Table 1.5. Comparative cost analysis of the membrane used in microbial fuel cells	60
Table 3.1. Comparison of mini MFC types according to configuration, anode volume, and response time	96
Table 3.2. Utilisation of microbial fuel for heavy metal removal cells (MFCs) in wastewater treatment.....	97
Table 3.3. Summary of types of membrane used in miniature MFCs according to their anode volume, surface area, the external substrate used, and their crossover study	103
Table 3.4. Properties of mini DCMFC equipped with Nafion and lab-fabricated PVA membrane	104
Table 3.5(a) Cost analysis of the lab-fabricated crosslinked PVA utilized in mini DCMFC.....	108
Table 3.5 (b) Cost Analysis of Smart Data Logger vs. Commercial Multimeter used in MFC experiment	108
Table 4.1. Summarises the different types of wastewaters used in the variable operation mode of the MFC system and the nutrient removal at certain conditions.....	131
Table 4.2. Electrochemical performance of the composite membrane and CA membrane-based MFC	136
Table 4.3. Breakdown of costs for the manufacture of the composite membrane	139
Table 5.1. A summary of the different membrane types used in miniature microbial fuel cells, considering factors such as anode size, surface area, type of fuel used, and how much material crosses between the chambers.....	159
Table 5.2. Properties of the modified membrane-based MFCs.....	163

Nomenclature

Abbreviations

MFC	Microbial fuel cell
ATR	Attenuated Total Reflectance
CA	Contact Angle
CV	Cyclic Voltammetry
BES	Bioelectrochemical Systems
DSC	Differential Scanning Calorimetry
COD	Chemical Oxygen Demand
DTG	Differential Thermo-Gravimetric
EB	Elongation at Break
EDX	Energy Dispersive X-ray Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transmission Infrared Spectroscopy
CS	Chitosan
NMP	N-Methyl-2-pyrrolidone
PFAS	Per and poly-fluoroalkyl
PVA	Polyvinyl Alcohol
OTR	Oxygen Transmission Rate
GO	Graphene Oxide
PBS	Phosphate Buffer Saline
UTM	Universal Testing Machine

TS	Tensile strength
HWW	Hospital wastewater
AFM	Atomic Force Microscopy
EIS	Electrochemical Impedance Spectroscopy
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
CE	Cellulose Ether
CA	Cellulose Acetate
GA	Glutaraldehyde
HPLC	High-performance Liquid Chromatography

Chapter 1: Introduction and Literature Review

1.1. Background and Motivation

Water is the most essential resource for maintaining life on Earth [1]. Despite over seventy-five per cent of the Earth's surface being water, less than one per cent is available for human use. For example, if the Earth's entire water amounted to 100 gallons, around 97 gallons would be saltwater (from oceans and seas), 2 gallons would be ice, 0.8 gallons would be groundwater, and just 0.2 gallons would be surface water in rivers, lakes, wetlands, and clouds. The restricted supply of freshwater has emerged as a significant worldwide issue [2]. Owa (2013) examined the origins, consequences, and potential remedies for water contamination [3]. Chaudhry and Malik (2017) delineated the main causes leading to water contamination, while Schwarzenbach et al. (2010) elucidated worldwide water pollution and its possible pollutants [4], [5]. Bashar et al. (2013) investigated the environmental hazards linked to water contamination [6]. A water crisis occurs when the demand for potable water surpasses the available supply in an area. In addition to water shortage, water pollution presents an even more significant danger to human health. It denotes the degradation of water quality due to hazardous pollutants, including chemicals and microbes [7]. Due to its status as a universal solvent, water readily dissolves several chemicals, rendering it particularly vulnerable to contamination [8], [9]. Prevalent contaminants include fluoride, nitrate, pathogenic bacteria, and trace heavy metals like cadmium, lead, chromium, nickel, zinc, arsenic, and mercury. Water contamination endangers natural equilibrium and human well-being. Rising concentrations of inorganic, organic, and microbiological pollutants present substantial threats to ecosystems and living species. Therefore, efficient strategies and resource distribution are crucial for managing and mitigating pollution [10], [11], [12]. Water contamination significantly contributes to the proliferation of waterborne illnesses,

including typhoid, cholera, and hepatitis. The ingestion of polluted water might result in grave repercussions for human health. Moreover, water pollution results in the deterioration of aquatic ecosystems and upsets the natural food chain, especially when people ingest aquatic species that have accumulated toxins. The release of untreated wastewater into the environment contaminates water bodies and presents considerable health hazards when ingested. In recent years, emerging contaminants (ECs) such as medicines, personal care products, plasticizers, surfactants, flame retardants, nanomaterials, and pesticides have attracted significant attention owing to their persistence and potential environmental hazards. Emerging pollutants exist at trace levels that are sometimes difficult to detect; yet, many are prevalent even in drinking water. Although several pollutants have been found, continuous study persists in revealing new emerging contaminants owing to their significant threats to human health and the environment. Due to their persistence in natural ecosystems, the total elimination of these toxins may be essential to safeguard both human and ecological health. Adsorption is being widely used as an effective, economical approach for mitigating pollutants. Numerous studies have thoroughly investigated emerging contaminants (ECs) and their environmental consequences. Richardson and Kimura et al. (2017) examined several emerging contaminants (ECs) and their prevalence, while Rodríguez-Narváez et al. (2017) investigated their origins, impacts, and the efficacy of current treatment methods [9]. Noguera-Oviedo and Aga (2016) enhanced the comprehension of the pervasive occurrence of emerging contaminants (ECs) and underscored the need of accounting for transformation products and metabolites [13]. These studies combined underscore the need for innovative detection techniques and expose the inadequacies of even sophisticated treatment procedures in entirely eliminating target pollutants. Rout et al. (2021) succinctly outlined the environmental repercussions of emerging contaminants, highlighting that existing wastewater treatment facilities, although functioning as the principal safeguard, are insufficient [13]. Municipal wastewater is a major conduit for the introduction of emerging contaminants

(ECs). Common personal care items, including nail polish, lipsticks, sunscreens, lotions, and insect repellents, often infiltrate wastewater systems post-application. Furthermore, medications and artificial sweeteners are metabolised in the human body and then excreted via urine, thereby increasing the concentration of emerging contaminants in municipal wastewater. The pharmaceutical and biomedical sectors generate substantial waste streams including bioactive substances, including diverse medications (antibiotics, analgesics, antidepressants, etc.), as well as their unutilized precursors and production by-products. Although the biological activity of the primary medicinal chemicals is well established, there is a paucity of knowledge on the chemical, physiological, and antimicrobial characteristics of their intermediates and byproducts. Furthermore, waste streams may include illicit substances, synthetic or natural hormones, steroids, and other novel pollutants. Consequently, it is essential to meticulously monitor and evaluate their environmental effect, ensuring that these waste streams are properly processed before disposal [14]. Perchlorinated compounds are extensively used as dirt- and grease-repellent agents in coatings and sprays for leather, textiles, and in polytetrafluoroethylene (PTFE) or Teflon-based non-stick cookware. Nonetheless, their persistence and accumulation in the environment provide considerable ecological hazards, notably endangering microbial ecosystems and interrupting normal biodegradation processes [15]. Organic solvents, herbicides, fungicides, insecticides, plant growth regulators, bactericides, and defoliants are emerging contaminants (ECs) from industrial sources that may infiltrate the environment, pollute surface water, and ultimately bioaccumulate in the food chain [16]. Agriculture accounts for more than 70% of the world's freshwater use (UNESCO-WWAP, 2003). In areas experiencing freshwater shortages, processed sewage and industrial effluent function as alternate irrigation supplies for agricultural output [17]. While wastewater irrigation alleviates water scarcity and disposal challenges, it may adversely affect crop production, quality, and soil health (Wang et al., 2007) [18]. Excessive organic matter accumulation

diminishes soil oxygen availability owing to microbial aerobic breakdown (Ajwa and Tabatabai, 1994) [19]. Thus, the U.S. Environmental Protection Agency (EPA) limits the average weekly Biological Oxygen Demand (BOD) application rate for land-applied wastewater to 112 kg/ha/day (John and Bauder, 2007) [20]. The increasing worldwide energy demand, propelled by rapid urbanization and industrialization, has resulted in a concerning rise in the combustion of fossil fuels, including coal, oil, and natural gas. This process emits significant quantities of greenhouse gases, including carbon dioxide, methane, and nitrous oxide, into the atmosphere. These gases entrap heat, exacerbating the greenhouse effect and resulting in the elevated global temperatures phenomenon central to climate change. Fossil fuels, accounting for over 80% of worldwide energy use, significantly contribute to increasing atmospheric carbon dioxide concentrations and the intensification of global warming. [21]. Humanity now confronts the significant issue of reconciling energy demands with environmental sustainability. In response, global initiatives are underway to shift towards cleaner energy sources, enhance energy efficiency, and advocate for sustainable urban development. Hence, the search for alternative energy sources that are both cost-effective and environmentally friendly has become an urgent necessity [22]. Among the world's 7.2 billion people, around 2 billion lack access to fundamental sanitation, and an additional 2 billion are denied safe and clean drinking water [23]. Supplying potable water directly to urban residences has grown more costly and is hastening the exhaustion of our limited fossil fuel resources [24]. Hospitals use significant quantities of water across diverse units and services based on their particular operations, resulting in the production of considerable volumes of wastewater [1]. The volume and attributes of hospital wastewater (HWW) are determined by variables like hospital size, the number and kind of wards or units, available services (e.g., kitchen, laundry, air conditioning), and institutional management procedures and awareness levels [16]. Hospitals in rich nations often create between 400–1200 liters of wastewater per bed daily, but those in underdeveloped nations

generate roughly 200–400 liters per capita daily. Domestic wastewater production typically varies from 100 to 400 liters per capita per day [25], [26], [27], [28], [29]. In several poor nations, hospital effluents are often pumped into municipal sewage systems and then discharged into adjacent water bodies without sufficient treatment, so presenting significant threats to public health [30], [31]. Hospital effluents include a diverse array of pollutants, demonstrating inherent toxicity levels 5–15 times greater than standard urban wastewater, thus impairing the functionality of activated sludge in traditional treatment facilities [32] [33]. Consequently, the management of hospital wastewater (HWW) and healthcare waste to mitigate possible dangers to adjacent populations continues to be a significant problem for healthcare institutions. Growing data indicates that insufficient hazardous waste water treatment systems may promote the spread of antibiotic-resistant microorganisms into the environment [34] [35]. Entities that release wastewater into municipal sewage systems are termed indirect dischargers, while those that discharge directly into rivers or surface water bodies are classified as direct dischargers. The majority of hospitals are classified as indirect dischargers [36] [37]. If inadequately handled, these wastes may significantly threaten ecological balance and human health, possibly resulting in communicable disease outbreaks, diarrhea epidemics, water contamination, and radioactive pollution [38] [39]. Urine and faeces from patients in specialized wards, such as oncology, often exhibit heightened concentrations of antibiotics, cytotoxic drugs, their metabolites, and X-ray contrast media, accounting for around 50%–80% of the overall hazardous burden in hospital wastewater [40] [41][42][43].

Consequently, guaranteeing a sustainable long-term energy supply in conjunction with efficient wastewater treatment has become an imperative need. The substantial potential of using microorganisms to extract valuable resources from waste via biodegradation has sparked considerable interest in microbial fuel cell (MFC) technology, providing a

sustainable method for waste management and energy recovery. Microbial fuel cells (MFCs) are bio-electrochemical devices that convert the reducing power generated during microbial metabolism into useful electrical energy. MFC technology facilitates the transition from a linear economy characterized by "make–use–dispose" to a circular one by converting trash into a valuable resource while concurrently generating clean electricity. In the linear model, wastewater and organic wastes are regarded just as undesirable by-products and disposed of, often incurring significant environmental and economic consequences. Conversely, MFCs use the metabolic processes of microbes to extract energy from waste, generating electricity or biohydrogen, while simultaneously facilitating nutrient recovery (e.g., nitrogen, phosphorus) and water reclamation. This terminates many resource cycles: trash transforms into feedstock, energy is produced on-site, and precious materials are reclaimed instead of discarded, as shown in **Figure 1.1**. This integration reduces dependence on fossil fuels, curtails waste production, and fosters sustainable urban and industrial systems, fundamental tenets of the circular economy [44]. Microbial fuel cells (MFCs) are bioelectrochemical devices that decompose organic substances while concurrently harnessing renewable energy from them. They provide a viable alternative to traditional power-generating technologies, especially for small-scale applications. In contrast to conventional systems, MFCs obviate the need for intermediary energy conversion devices, hence streamlining operation and reducing related expenses. They have a greater theoretical energy recovery potential, since their efficiency is not limited by the Carnot cycle, allowing for more direct and effective energy extraction. MFCs promote sustainability by mitigating the emission of greenhouse and hazardous gases during operation. Moreover, their capacity to diminish waste production amplifies their environmental advantages. MFCs, with their synergistic benefits, emerge as a sustainable technology for the conversion of solid organic waste into clean, renewable energy.

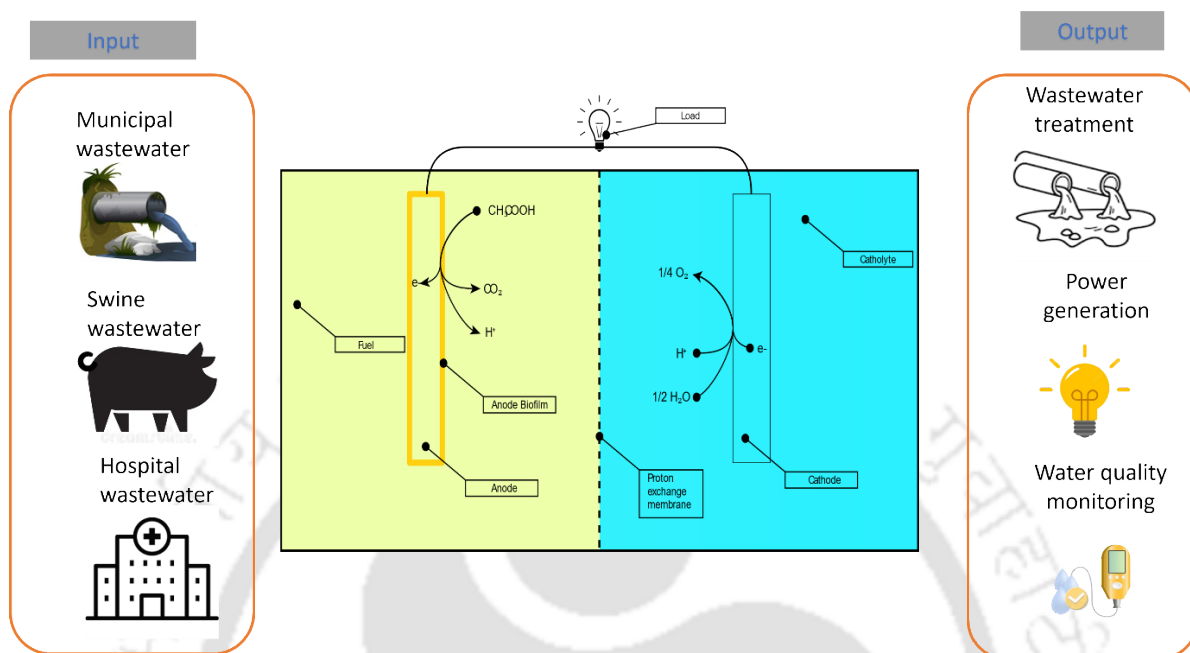


Figure 1.1. Schematic of different feedstocks as effluent in microbial fuel cells for power generation

1.1.1. Revolutionizing MFC Design: Innovations in Architecture

In recent decades, researchers have investigated several techniques to improve the efficiency and reliability of microbial fuel cells (MFCs). Various MFC topologies have been examined to enhance power production and optimize wastewater treatment efficacy. Recent research has concentrated on enhancing cathode structures, including innovations like rotating air cathodes and dual gas diffusion cathode designs, to improve MFC performance [45]. Other endeavours have been made to encase the cathode with biofilm, which catalyses the reduction process in microbial fuel cells (MFCs) [46]. A significant obstacle impeding the extensive use of MFCs is the efficiency decline seen with process scale-up. Jadhav et al. have created a scalable, stacked bioelectric toilet MFC with a 100 L capacity, which can power different electrical gadgets and charge mobile phones using an integrated sophisticated power management system (PMS). This device shows the capability to process roughly 87–92% of

the organic materials included in septic tank effluent. Hiegemann et al. recently combined four single-chamber, membrane-less microbial fuel cell units to create a 45 L prototype system, which was effectively operated under real-world circumstances [47]. During a nine-month operating period, the system attained a coulombic efficiency of 24.8%, accompanied by significant reductions in COD and total suspended solids (TSS). The anodic chamber, functioning under anaerobic circumstances, promoted the proliferation of exoelectrogenic bacteria adept at effective extracellular electron transfer [48]. The design and development of MFCs amalgamate elements from materials science, microbiology, and engineering. Researchers are enhancing the scalability and performance of microbial fuel cells (MFCs) for effective wastewater treatment and sustainable energy production by optimizing structural components and system configurations.

1.1.2. Development in Single-chambered Microbial Fuel Cell

This microbial fuel cell (MFC) configuration eliminates the need for aeration or external oxygen supply by employing a single chamber the anode, while exposing the cathode directly to the ambient environment. Such a simplified setup enables both batch and continuous modes of operation. **Figure 1.2** illustrates a streamlined version of the single-chamber microbial fuel cell (SCMFC), representing an efficient and cost-effective system for generating electricity through microbial degradation of organic matter. In an SCMFC, the anode and cathode are typically positioned within the same chamber, either separated by a minimal barrier or left without one. This design significantly reduces internal resistance, fabrication complexity, and overall system cost. Electrogenic microorganisms colonize the anode surface and oxidize organic substrates under anaerobic conditions within the wastewater or feed solution. During this process, electrons released from microbial oxidation are transferred to the cathode via an external circuit, generating an electric current. Concurrently, protons migrate through the proton exchange membrane (PEM) or electrolyte

to the cathode, where they combine with oxygen and electrons to form water or other benign products. This continuous electron flow sustains bioelectricity generation. The simplicity and robustness of the single-chamber design make SCMFCs highly suitable for diverse applications, including wastewater treatment, environmental monitoring, and decentralized or remote power generation. Min and Logan [48] developed a fundamental flat-plate MFC using a non-conductive polycarbonate plate measuring $15 \times 3 \times 15$ cm (L $\times$ H $\times$ B). In single-chamber MFCs, using an air cathode might diminish coulombic efficiency (CE) since it facilitates the diffusion of oxygen from the cathode to the anode, hence interrupting the completely anaerobic conditions essential for optimum microbial activity [49]. The availability of oxygen offers bacteria an alternate electron acceptor, which they are unable to use for current generation. Consequently, microbial cells in a microbial fuel cell (MFC) are often sustained at entirely anoxic conditions to guarantee exclusive electron transport to the anode [50]. The single-chamber design is one of the most straightforward to scale, since it uses ambient air for oxygen and needs less materials overall [51]. This arrangement may accommodate different electrode morphologies, such as brush, granular, and plane, because the chambers for the anode and cathode are independent of one another.

1.1.3. Double-chambered Microbial fuel cell

A dual-chamber microbial fuel cell (DCMFC), as indicated by its nomenclature, has distinct anode and cathode compartments separated by a salt bridge or a proton exchange membrane (PEM) [52]. **Figure 1.3** illustrates that the PEM or another ion-selective separator facilitates proton transfer while reducing substrate and oxygen crossing. The anode chamber creates an anaerobic environment in which microorganisms oxidize organic substrates, yielding electrons and protons. Electrons are transmitted extracellularly to the anode by direct electron transfer (DET) processes, producing current and voltage as they traverse an external resistor or load

before arriving at the cathode in the oxygen-rich chamber. Concurrently, protons traverse the PEM to the cathode, where they react with oxygen and electrons in a four-electron oxygen reduction reaction (ORR), yielding water and finalizing the circuit. The dual-chamber design improves regulation of redox conditions, reduces oxygen penetration into the anode (thereby reducing electron loss), and facilitates selective proton transfer. These benefits enhance the overall operating efficiency of the MFC, rendering DCMFCs appropriate for environmental monitoring, wastewater treatment, and renewable energy production. Typical electrode materials are carbon paper, graphite fibre brushes, stainless steel mesh, copper, graphite, and carbon cloth [53]. To sustain anaerobic conditions in the anode chamber, a continual supply of nitrogen is often necessary. Logan and associates constructed a conventional H-type microbial fuel cell using 300 mL borosilicate glass containers linked by a secured glass bridge and partitioned by a Nafion membrane [54]. Carbon paper served as both the anode and cathode electrode, with the cathode coated in a platinum catalyst (0.35 mg/cm^2). Upon elevating the cysteine content to 0.770 g/L , the highest power density increased from 19 mW/m^3 to 39 mW/m^2 . Despite the limitations of scalability and cost, these improvements illustrate the considerable promise of double-chamber MFCs for sustainable energy production and wastewater treatment applications.

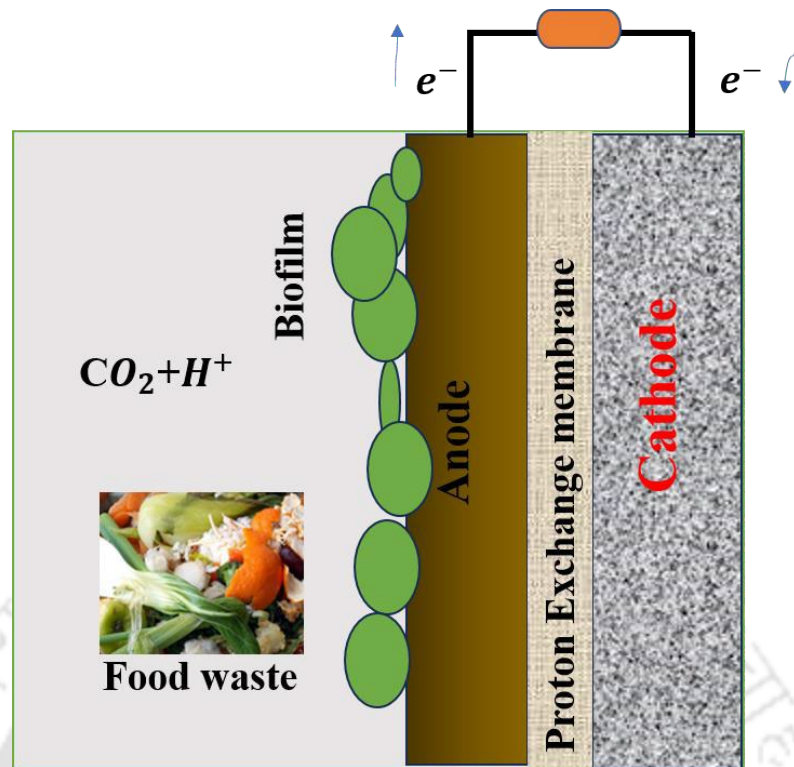


Figure 1.2. Single-chambered microbial fuel cell

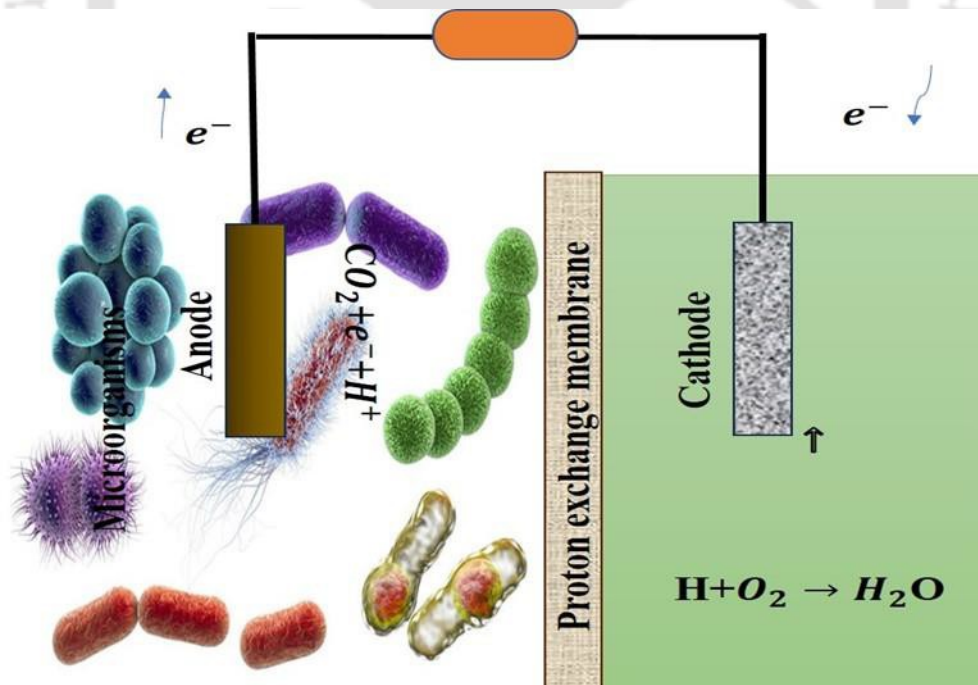


Figure 1. 3. PEM-based microbial fuel cell

1.1.4. Litre-scale MFC setup

Numerous recent evaluations have concentrated on electrodes, addressing their composition, performance, cost, application scope, and surface modification methods.[55]. Moreover, current developments in separator materials have been investigated, assessing their performance based on substrate permeability, proton conductivity, and oxygen transfer efficiency [56][57]. Research has also investigated the impacts on coulombic efficiency, power density, and internal resistance. Millilitre-scale microbial fuel cells have exhibited markedly elevated volumetric power densities, achieving levels in the order of KW/m³ in optimal configurations, which is normalised to reactor volume as defining electrode surface area in a micron-scale system poses challenges [58]. Additionally, reactor performance in miniaturised MFC system is not only governed by electrode surface area but also substrate concentration, hydraulic retention, and mass transport limitation, which are volume-dependent parameters [1], [2] [3], [4]. Although scaling MFCs to commercial levels presents challenges, the biggest MFC systems documented in the literature show considerable advancement [59] were 0.52 to 1.27 L MFC. MFC power densities ranging from 9 to 32 W/m² and volumetric current densities of 39 to 103 A/m³ MFC are typical values for these reactors. Larger microbial fuel cells are often considered to demonstrate reduced efficiency owing to heightened ohmic losses and elevated electrode overpotentials [60][61]. Statistical evaluations and meta-analyses of the literature have provided significant insights into effective operational techniques for microbial fuel cells (MFCs) [62]. This research has focused on the critical factors influencing reactor size and operational techniques that impact wastewater anodic treatment [63]. On the other hand, it is essential to assess new developments meant to reduce performance reductions in two-chamber microbial electrochemical systems (MES) at the pilot scale, considering the significant interdependencies among these systems. Furthermore, a more thorough analysis is needed to

determine the scaling potential of the dual-chamber MFC System.

1.1.5. Millilitre scale MFC set up

Millilitre-scale devices provide an effective method for investigating the relationship between device design and active bacteria to address fundamental challenges in electron transport at the microbial/anode interface. [64]. Their adaptability in implementing designs that lower their internal resistance and improve mass movement is the reason for this. There is a study on a 1.2-millilitre mini-MFC chamber with a high surface area to volume (SAV) ratio to encourage proton diffusion and a high-power density of 500 /m^3 . Furthermore, a 2.5-ml air-breathing MFC has been shown to have a power density of 1010 [65]. Millilitre-to-litre MFCs possess a little volume and commendable power output, making them appropriate for portable power applications. This is especially applicable when they are arranged in sequence to provide more power and voltage [66]. Microfluidic Microbial Fuel Cells (MMFCs) enhance the performance of MFCs by offering precise control over fluid dynamics in microenvironments. This technique has shown promising results regarding accuracy and cost-effectiveness [67]. MMFCs provide a unique platform capable of powering miniature electronic devices such as wireless networks and implantable pacemakers. They may further function as biosensors, rapidly identifying germs and detecting toxicity in water [68]. MMFCs combine various components, including electrodes, membranes (if required), and fluid control devices, into a fully functional platform with volumes as small as a few hundred microliters. MMFCs can be stacked to boost power density, which may enable applications that need larger power outputs. Due to this, MMFC technology offers a versatile and scalable solution for environmental and biological applications. In bigger tube-shaped MFCs, the anode is usually a tube that is electrically separate from the cathode by a separator. The tubular structure is often made up of different types of cylindrical materials, like polyvinyl chloride [69], and a tube-shaped cation exchange membrane. A separator material surrounds the anode's chamber to keep it from touching the

cathode. After that, the separator goes around the cathode. Joining more tubular MFC units in series by stretching the tube made it easier to scale up. This was because many tubular designs were used in continuous flow mode, which made an MFC stack. Research shows that the tubular design reduces dead space in the reactor and keeps the cross-section dimension close to optimal during scale-up [70]. This helps create a steady-state, well-mixed flow regime that is close to plug flow. There have been fewer studies on MFCs with flat-plate designs than on those with tubular designs. A separator material surrounds the anode's chamber to keep it from touching the cathode. After that, the separator goes around the cathode. Joining more tubular MFC units in series by stretching the tube made it easier to scale up. This was because many tubular designs were used in continuous flow mode, which made an MFC stack. Research shows that the tubular design reduces dead space in the reactor and keeps the cross-section dimension close to optimal during scale-up. This helps create a steady-state, well-mixed flow regime that is close to plug flow. There have been fewer studies on MFCs with flat-plate designs than on those with tubular designs. Wastewater Generation and Treatment Challenges. A critical problem of the 21st century is guaranteeing universal access to clean and enough water. Approximately 2.6 billion people in poor countries continue to lack access to clean drinking water and sufficient sanitary facilities[71]. The United Nations World Water Development Report indicates that the industrial sector accounts for 22% of worldwide freshwater consumption, with utilization varying from 59% in high-income countries to 8% in low-income nations [72]. Worryingly, only 24% of the wastewater produced by homes and enterprises is treated before disposal or reuse. Accelerated urbanisation, population expansion, and lifestyle changes are exacerbating wastewater discharge, imposing significant strain on aquatic ecosystems [73]. Wastewater generally comprises a complex amalgamation of organic and inorganic substances, heavy metals, and toxic chemicals. This escalating pollution jeopardises the equilibrium of natural ecosystems and interferes with vital biogeochemical cycles, mostly influenced by microbial metabolic processes [74] [75]. India, comprising 17% of the global

population, is anticipated to exceed 1.5 billion residents by 2050, based on the current annual growth rate of 1.2%. The nation comprises just 2.45% of the world's surface area and 4% of the Earth's natural water resources [76] [77]. Extensive regions of agricultural land and aquatic ecosystems are now tainted by contaminants originating from geogenic sources, agricultural activities, and industrial discharges [78] [79]. Despite the global utilisation of diverse treatment technologies such as activated sludge processes, trickling filters, fluidised aerobic bioreactors, and membrane separations, their substantial capital, operational, and maintenance expenses render them unsustainable for large-scale implementation [80]. A variety of wastewater treatment methods have been created to provide alternative water sources, responding to the rising worldwide water demand. Nonetheless, attaining efficient resource recovery using these methods continues to pose a considerable barrier [81]. Choosing the most appropriate wastewater reclamation method necessitates optimising the equilibrium of environmental, social, and economic factors [82]. The elimination of developing pollutants and harmful microorganisms may be achieved by the use of new treatment strategies, such as enhanced oxidation processes, adsorption techniques, membrane technologies, and filtering methods [82].

1.1.6. Anaerobic and aerobic treatment processes

The anaerobic decomposition of organic waste in lagoons or reactor systems eliminates the need for aeration, leading to reduced energy consumption and minimum sludge generation. Nonetheless, these procedures are somewhat sluggish and, when used in isolation, often prove inadequate for attaining the needed decrease in organic load. Therefore, an additional aerobic therapy phase is often necessary. The predominant anaerobic technology used in breweries is the vertical upflow UASB (Upflow Anaerobic Sludge Blanket) reactor. In this arrangement, granular anaerobic sludge (1–4 mm) is suspended inside the reactor, while the influent wastewater is pushed upward from the base. Microorganisms decompose remaining substrates,

resulting in the production and accumulation of biogas in the top area of the reactor, accompanied by granular sludge and wastewater. A three-phase separator, or gas–liquid–solid separator, is put at the top to segregate biomass, biogas, and treated effluent. The commonly used method is the fluidised bed reactor (FBR), in which wastewater ascends at speeds ranging from 10 to 20 m/h. FBRs are especially effective for wastewater that contains soluble or readily degradable organic substances, such as brewery effluent. The increased upward flow enlarges the support medium, usually sand or activated carbon, upon which active anaerobic biomass exists. As the wastewater traverses the fluidised bed, interaction between the substrate and biomass promotes biogas generation, which is captured at the upper section of the reactor.

1.1.7. Recent Nature-inspired innovation in membranes to enhance performance

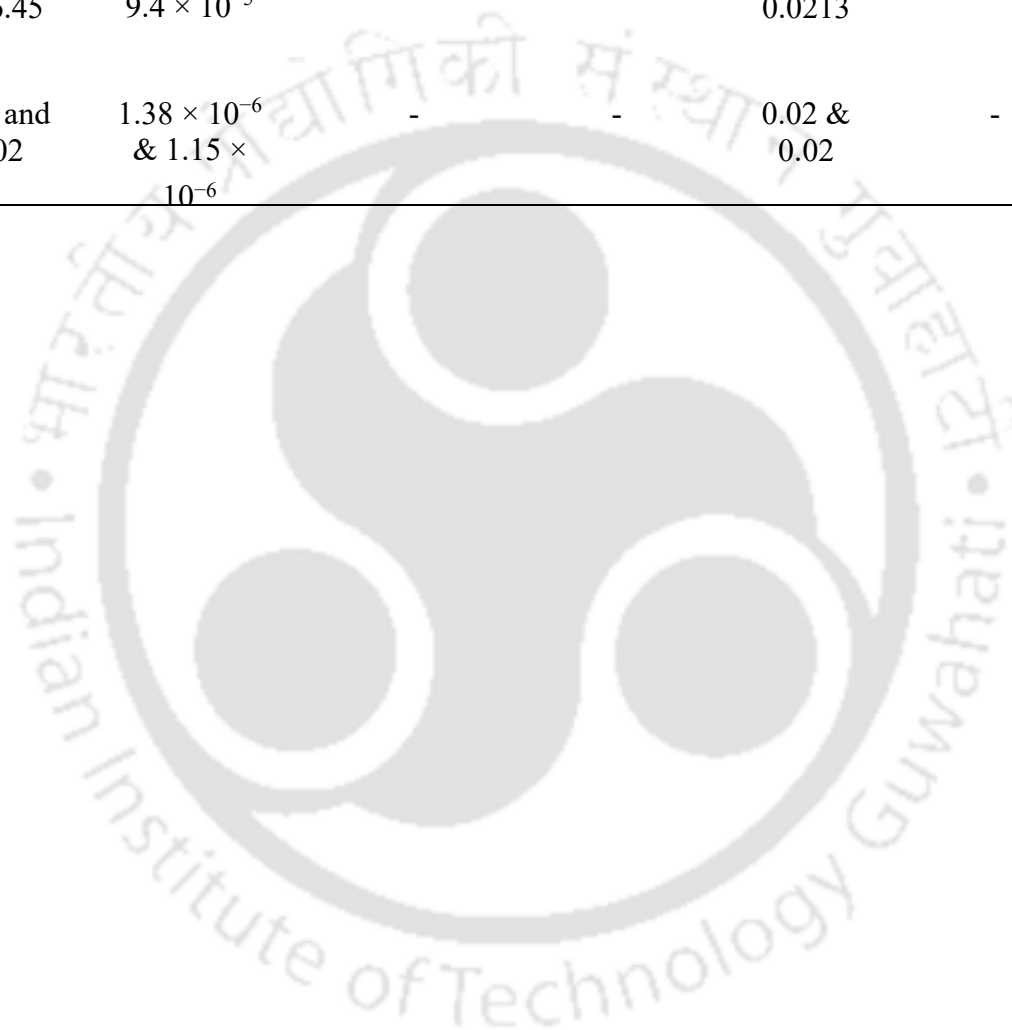
Protons are transported from the cathode to the anode of an MFC more easily when a membrane separates the two reactions [83]. This membrane serves as a mechanical barrier, preventing the transfer of oxygen from the aerated cathode to the anaerobic anode chamber, therefore delineating the two chambers of the anode and cathode [84]. Membranes, typically composed of polymers, are suitable for MFC applications if they possess specific critical attributes, including low internal resistance, efficient mass transfer, robust long-term viability, prolonged cycle life, energy recovery, high ionic conductivity, minimal substrate loss, resistance to biofouling, presence of oxygenated water in the cathode, an anaerobic anode, and temporal stability [85]. Table 1.1 delineates the primary characteristics and components of PEM-based MFCs, including details on their materials, operation, and the latest advancements in the industry. The proton exchange membrane-based microbial fuel cells. A significant category of polymeric membranes is ionic exchange membranes (IEMs), distinguished by the presence of functional groups in their structure that enable the exchange of anions and cations. These membranes impede the passage of co-ions while permitting the transport of counter-ions [86].

Ionic exchange membranes can be categorized into five distinct types: Mosaic Ion exchange membranes (IEM), Bipolar membranes (BPMs), Anion and cation exchange membranes, amphoteric ion exchange membranes (IEMs) [87]. To produce a net negative functional group charge, CEMs, also known as PEMs, are made to make it easier for protons and other cations to enter the cathode and pass through the membrane chamber [88]. In anion exchange membranes charge transport is enabled by movement of anions like OH^- , Cl^- , HCO_3^- through fixed positively charged functional groups. Buffer ions can function as mobile charge carriers. [89]. As Nafion membrane substitutes in MFCs, several substitutes, most notably membranes made of non-fluorinated hydrocarbon polymers, have attracted an abundance of interest. To increase the ability of protons of non-fluorinated hydrocarbon membranes and open channels for the passage of hydrate (H_3O^+) across the membrane, sulfonation has been used [90]. This method has been used to create affordable substitute proton exchange membranes (PEMs) for MFCs using polyarene ether sulfones (PAES), polybenzimidazole (PBI) [65], polyimide (PI), and poly(ether ketone) (PEEK) are examples of hydrocarbon polymers [91]. Research has indicated that the density of power of 58.726 mW/m^2 generated by sulfonated polyether sulfone mixed with polyether sulfone membrane in MFCs surpasses that of the membrane Nafion in MFCs (45.512 mW/m^2) [92].

Table 1.1. Some of the investigated PEM-based Microbial fuel cells

PEM	PD (mw/m ²)	O ₂ transfer (cm/s)	Internal resistance (Ω)	COD removal (%)	Thickness (μm)	Coulombic efficiency (%)	Conductivity (S/cm)	Ref.
Sulfonated poly (ether ether ketone)	77	10 ⁻⁶	-	-	180	64	0.163 x10 ⁻²	[93]
Sulfonated polybenzimidazole(S-OPBI)	110	-	-	-	-	-	0.0783	[94]
Cross-linked PVA-GO	140 ± 17	1.5 × 10 ⁻³	~5.4	~81.89	0.4	~1.32	~1.2 × 10 ⁻⁴	[95]
sulfonated polyether sulfone SPES/PES	58.726	3.26 x10 ⁻⁵	-	72	250	18	-	[96]
Nafion-112	19.7		2354	70	50.8	7.8	4.8 x10 ⁻²	[97]
PVA-Nafion-borosilicate	0.0068	3.3 ± 0.19 × 10 ⁻⁴	100	78 ± 4.8	167	35.3 ± 2.27	0.07	[98]
PVDF-g-PSSA	185	5.5 x10 ⁻⁶	228	75	80	-	0.046	[99]
Polyether sulphone	403.5	3.17 ± 10 ⁻⁵	-	-	140	92.8	-	[100]
Sulfonated PVDF-co-HFP/Nafion blended with nano alumina	541.52	9.27 × 10 ⁻⁴	-	-	200		3.57 × 10 ⁻²	[101]
Polybenzimidazole and polyvinylpyrrolidone blended membrane	231.8	-	-	-	-	-	1.2 × 10 ⁻³	[102]

Flemion	200	-	-	-	-	18.6	-	[103]
Sulfonated PVDF-coated Nafion 117	446.45	9.4×10^{-5}			0.0213		5.91×10^{-3}	[104]
SPEEK & GO SPEEK	812 and 902	1.38×10^{-6} & 1.15×10^{-6}	-	-	0.02 & 0.02	-	0.108×10^{-3} & 0.148×10^{-3}	[105]



1.1.8. Polymeric Membrane

A polyvinyl alcohol-Nafion-borosilicate membrane created by Tiwari et al. has been the subject of several research studies investigating Nafion-based materials for MFC purposes [106]. This membrane is economical and has produced a significant amount of power in MFC systems [107][108]. Furthermore, a hybrid membrane that replaces Nafion and has a maximum power density of 548 mW/m^2 is made of perfluorinated sulfuric acid ionomer-coated polyvinylidene fluoride nanofibers (PVDF-PFSA) [109]. Metal-organic framework and sulfonated polysulfone (SPSF/MIL-100(Fe)) were combined to create a composite polymer electrolyte membrane that, in a recent development, showed promising efficacy in MFC, achieving a power density of 27.60 mW/m^2 , 31.01% coulombic efficiency, from meat poultry wastewater [110]. However, because of their high cost of manufacture, extended breakdown period, and difficulty in reuse and recycling, synthetic polymers used in proton exchange membranes (PEMs) pose environmental issues. Because of their water absorption capabilities, ion exchange capacity, biocompatibility, renewability, sustainability, and environmentally friendly habits, natural biopolymers have become attractive substitutes for PEM for use in microbial fuel cells (MFCs) [111]. Considering many different forms of energy storage and conversion systems, such as MFCs, biopolymers, polyhydroxyalkanoates (PHA), polyhydroxy butyrate (PHB), cellulose, chitosan, starch, alginate, pectin, and gelatin [95] have attracted a lot of attention [112]. To improve membrane characteristics for MFC applications, a variety of changes to organic biopolymers have been investigated. These modifications include plasticization, grafting, and the addition or replacement of certain functional groups. By employing low-cost membranes, including dried agar from red algae as PEM, the overall power density of $20,000 \text{ mW/m}^3$ was attained, surpassing those achieved with MFCs. Nafion 11 (6800 mW/y by Sirajudeen et. al, an amalgamated PEM made from a solvent mix of medium-chain length PHA (mcl-PHA) and PHB in MFC had a higher power density of 912 mW/m^2 [113]. This composite PEM also had

70% COD elimination and 64% CE. Additionally, inexpensive food waste-derived sulfonated biochar has been combined with polyvinyl alcohol to act as a PEM to prevent membrane biofouling in MFCs and lower commercialization expenses [99]. Filtration technology is led by polymeric membranes because of their superior flexibility, outstanding film-forming skills, mechanical resilience, chemical stability, high perm selectivity, and capacity to transport specific chemical species. Their adaptability to a wide range of sectors is further enhanced by their affordability and capacity to customize pore sizes for distinct filtration processes. Membrane technology is a very successful method of treating water, making up as much as 53% of the methods used worldwide to produce clean water. It is a recommended option because of its ease of use, little or no requirement for chemical additives, cost-effectiveness, avoidance of phase transitions, high productivity, ease of scaling up, and high removal capacity. These benefits make membrane technology a valuable tool for treating wastewater and brackish water.

1.1.9. Sustainable bio-cellulose membrane

As the most common biological polymer on Earth, cellulose exists in the walls of the cells of plants, algae, bacteria, and fungi, among other creatures. It has the potential to be both biocompatible and renewable, making a wide range of uses possible. The structural components of cellulose are D-glucose units arranged in linear chains joined by β (1 $\rightarrow$ 4) bonds, which contain both crystalline and amorphous regions [114]. High hydrophilicity increased thermal and mechanical capabilities, and proton conductivity are just a few of the extraordinary features imbued in cellulose by its complex framework of hydrogen bonds both inside and between molecules. Thus, cellulose is usefully employed in the production of Microbial fuel cells (MFCs) that employ proton exchange membranes (PEMs) [115]. Numerous modifications have been employed to control membrane bloating and enhance durability, thermal endurance, proton conductivity, and quaternization for a variety of purposes. These

modifications include polymer mixing, crosslinking, sulfonation, quaternization, phosphorylation, and the insertion of inorganic particles[116]. Cellulose filter paper has two functions in the context of microbial fuel cells (MFCs): it acts as an electrode affirmer and a separator [117]. In recent work, proton exchange membranes (PEMs) in several MFC settings using *E. coli* bacteria were made using cellulose filter sheets with variable pore sizes and levels of thickness. There has been further investigation into the use of cellulose in MFC for power generation. Multi-walled carbon nanotubes (CNTs) and bacterial cellulose were mixed in a study by Mashkour et al. to produce a monolithic membrane electrode assembly (MEA). This MEA was then employed in a single-chamber MFC (SCMFC), where it outperformed earlier combinations [110].

1.1.10. Chitosan-based nanocomposite

Chitosan (CS) has emerged as a very appealing alternative for polymer electrolyte membranes in fuel cells due to its affordable price, hydrophilic qualities, biocompatibility as lack of toxicity, widespread accessibility, and great thermal and chemical durability [118][119]. Nevertheless, in wet conditions, the noteworthy hydrophilicity of CS might cause membrane swelling, which could jeopardize the mechanical durability and selectivity of the membrane. However, because chitosan contains easily manipulated amino and free hydroxyl groups, it may be without difficulty modified to get more effectively certain qualities that are suited for certain uses. The applications of chitosan in membranes have mainly been studied in the following forms: chitosan membranes that are self-cross-linked, blended using polymers (cellulose, alginate, nylon, polyvinyl pyrrolidone, polyacrylic acid, or polyvinyl alcohol); combined with inorganic nanoparticles to reduce membrane overlap and increase the membrane's strength, thermal stability, and proton conductivity; or chitosan/sulfonated polymer composite membranes respectively. Chitosan (CS) molecules' positive charge rises as

the quaternization length increases, attracting negatively charged microbial cell membranes to the CS membrane [120]. Because of this attraction, intracellular and proteinaceous materials seep out, inhibiting the development of microorganisms on the surface of the membrane. Consequently, quaternized CS membranes exhibit reduced membrane fouling.

1.2. Current trend of chitosan biopolymer as electrode base material in fuel cell

The catalytic particles in polymeric electrolyte-based fuel cell electrodes are usually either reinforced or unfounded on a substrate or gas diffusion sheet. Catalyst particles are frequently bound together, and ionic conduction is facilitated by binder materials, such as polymeric substances [121]. Despite being widely used as an electrode binding agent because of its advantageous characteristics as its ability to provide biomechanical support and promote catalyst dispersion, Nafion is costly and loses conductivity when it doesn't get enough hydration. On the other hand, because of its hydrophilic character and capacity to retain water, chitosan performs better as a binder than Nafion, particularly at higher cell temperatures. Furthermore, compared to Nafion, chitosan uses less binder material. By using aldehyde compounds, Klotzbach et al. created tweaked chitosan membranes that are biodegradable, hydrophobic, as well as biocompatible. In sensor and fuel cell applications, these membranes can be used as Nafion substitutes for electrode coatings [122]. Since biopolymers are environmentally benign, there is an increasing interest in using them in wastewater treatment, particularly in biopolymer composites. Due to the growing need for environmentally friendly products, bio-flocculants have become a viable substitute for conventional flocculants. Biopolymers have various benefits for treating wastewater, including increased efficacy and efficiency. They efficiently eliminate organic debris, heavy metals, and suspended particles from wastewater, lessening the discharge's negative environmental effects. Utilizing biopolymers also facilitates the recycling and reuse of waste materials, which is in line with

the concepts of a circular economy. All things considered, biopolymers offer an economical, practical, and sustainable wastewater treatment option that greatly reduces the environmental impact of treated water outflow. The several uses of biopolymers in microbial fuel cells (MFCs) are depicted in **Figure 1.4** below. These uses demonstrate the adaptability and environmental friendliness of biopolymers in improving MFC performance and sustainability.

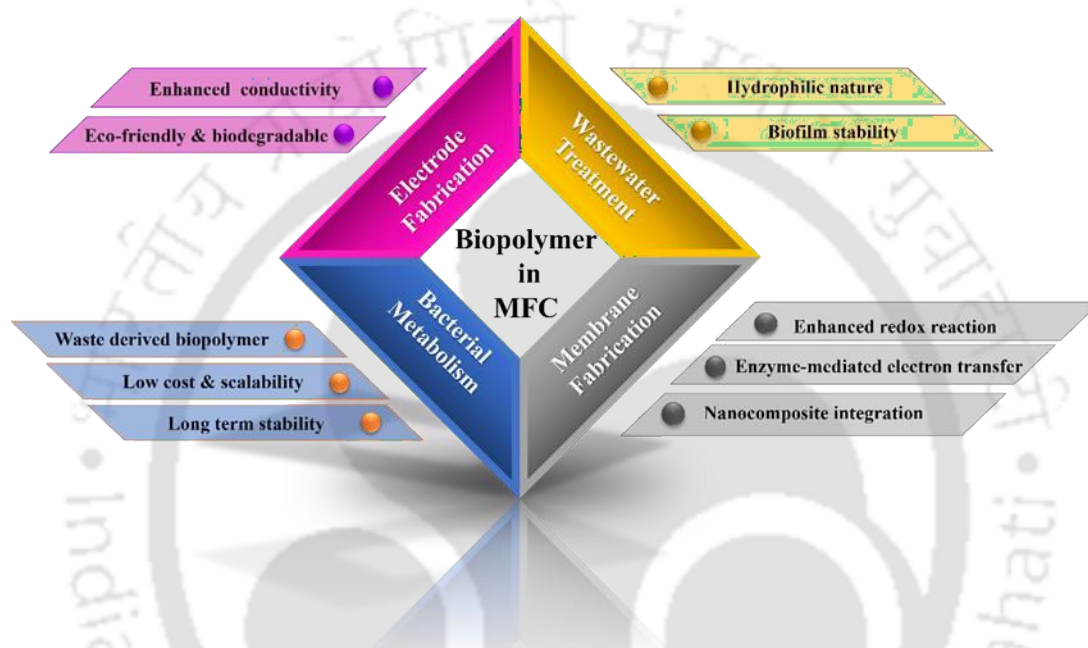


Figure 1.4. Application of Bio-based polymeric materials in microbial fuel cell technology

1.2.1. Factors to improve microbial Diversity and Population dynamics of MFC

Recent research has considerably expanded the diversity of bacteria identified as capable of functioning in microbial fuel cells, which are electrochemically active devices for energy generation. These organisms, known as "anode-respiring bacteria" or "exoelectrogenic bacteria," have been shown to autonomously produce and transmit electrons from substrates to a functioning electrode without the involvement of intermediaries [123]. Enhancing power output, essential for realizing the potential applications of microbiological fuel cells, will be

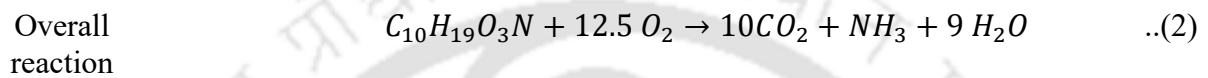
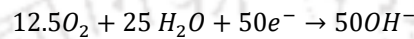
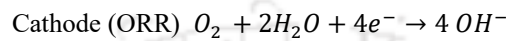
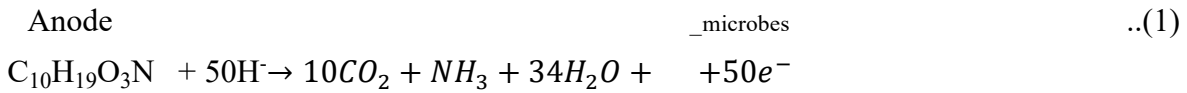
facilitated by a deeper understanding of the microbial community and electrochemically active bacteria in MFCs. The anode of a microbial fuel cell (MFC) hosts exoelectrogenic microorganisms that facilitate the biological transformation of diverse feedstocks into electrical energy [124]. Significant progress has been achieved in comprehending physical structure, genetic potential, and metabolic capacity related to the generation of MFC electricity. Gram-negative bacteria, mostly comprising the exoelectrogenic bacteria of microbial fuel cells (MFCs), are classified under the phylum Proteobacteria. The influence of the differences between Gram-positive and Gram-negative bacteria on the electrogenic activity and performance of the former remains unresolved [125]. Studies on Gram-negative bacteria have also substantially contributed to our current understanding of anodic electron transfer mechanisms, such as self-mediated electron transfer via endogenous redox-active metabolites or direct electron transfer via membrane-bound c-type cytochrome and nanowires. So far, from MFCs, about fifty exoelectrogenic bacteria have been isolated and identified. Phylogenetic analysis indicates that these exoelectrogenic bacteria are members of the phyla Acidobacteria, Bacteroidetes, Firmicutes, and all five classes of Proteobacteria. Shortly, more exoelectrogenic bacteria found within MFCs ought to be located, recognized, and examined.

1.2.2. Microbial Electron Transfer Mechanism

Oxidation and reduction reactions take place in Microbial Fuel Cell (MFC) systems, and the system's ability to accept electrons (reduction) or contribute electrons (oxidation) can be measured using the Oxidation-Reduction Potential (ORP). Exoelectrogenic (also known as electrogenic or electroactive) bacteria that have been anaerobically digested and adhered to the anode carry out the oxidation reaction. By oxidizing substrates with low redox potentials and releasing or donating electrons in the process, these microbes obtain energy. An external electrical circuit transports these electrons to the cathode, where a final electron acceptor with a greater positive redox potential reduces them [126]. The ability of the microbes to quickly

regenerate and adapt to new environments and substrates is one benefit of these systems.

Utilizing Wastewater. **Figure 1.5** shows the mechanism of electron transfer in a microbial fuelcell.



Extracellular electron transport is frequently facilitated by the electrons liberated during the anaerobic digestion of exoelectrogenic bacteria (EET) [127]. Electron transfer (ET) is made possible by this process between the intracellular metabolism of living systems and exterior solid materials, which are non-living systems, such as electrodes or minerals. Since electron transmission is directly related to the generation of electricity in microbial fuel cells (MFCs), the conductivity of the biofilm is essential for high energy output. While our understanding of the mechanisms underlying electron transfer has improved over the last ten years, it is now widely accepted that a variety of physiological mechanisms are at play. Mediators, shuttles, pili-nanowires, and membrane-bound processes are a few examples of these mechanisms [128].

1.2.3. Powerhouse Innovation of microbial fuel cells

Regarding the microbial fuel cells (MFCs) we propose to deploy, optimizing the production of electricity is critical, and this necessitates a thorough understanding of the electrochemically active bacteria and microbial communities within MFCs. Using suitable and efficient research methods is essential to achieving this, especially in light of the continually changing microbiological techniques and procedures. Although cooperation among researchers might alleviate some obstacles in microbial investigations inside MFCs, it is still necessary for

individual researchers to understand how to identify methodological constraints, analyze data, and talk about the consequences of those findings. In the case of microbial community analysis, for instance, the intricacy and inappropriate use of molecular methods may result in variable and inconsistent outcomes, raising the possibility of erroneous or biased study findings [129]. To further our understanding of the microbial activities inside MFCs, several review publications on microbiology in MFCs have emphasized the significance of methodological rigour and critical interpretation of data. Because of their easier maintenance requirements and greater flexibility to different feedstocks, mixed bacterial cultures have been preferred over pure cultures [130]. Numerous investigations have demonstrated a correlation between MFCs' exceptional performance and a functional mixed population that is primarily made up of exoelectrogenic microbes. The microbial fuel cells (MFCs) use exoelectrogenic microorganisms to colonize their anode and convert different substrates into electrical energy. Through several approaches, significant progress has been made in understanding their morphology, genetic potential, and metabolic capacity, which are critical for generating electricity in MFCs. Removing an exoelectrogenic bacterium in pure culture coming from bioelectrochemical systems (BESs) or microbial fuel cells (MFCs), where the bacteria are most likely to flourish and multiply, is frequently crucial to knowing the bacterium in detail [131]. Although a large number of pure strains were previously isolated from non-BES settings, such as wastewater treatment facilities and sea sediment, it has since been demonstrated that they display electrochemical activity. Within the phylum Proteobacteria, the majority of the exoelectrogenic bacteria found in microbial fuel cells (MFCs) are categorized as Gram-negative bacteria. Notably, studies have been conducted on *G. sulfurreducens* and *S. oneidensis* as model exoelectrogens in detail. *Escherichia coli*, *P. aeruginosa*, and *Rhodospirillum rubrum* are a few more often found Gram-negative bacteria [132]. Although much of the initial study was on Gram-negative bacteria, the identification of the capacity of Gram-positive bacteria to produce electricity in MFCs has been further investigated in later research. The

"gold standard" for distinguishing between pure bacterial cultures and microbial communities' architectures is 16S rRNA-gene sequencing. Thus far, over fifty exoelectrogenic bacteria have been found and successfully extracted from microbial fuel cells (MFCs). These exoelectrogenic bacteria include members of the phyla Acidobacteria, Bacteroidetes, Firmicutes, and all five classes of Proteobacteria, according to a phylogenetic study. In the not-too-distant future, exoelectrogenic bacteria from MFCs may proliferate, be identified, and be studied.

1.3. Microbial catabolic activity of microorganisms

Although MFCs may function with pure bacterial cultures, actual applications for energy production from organic waste often depend on naturally existing microbial communities. Anaerobic sludge is the predominant inoculum used [133], [134], but wastewater and soil have also been applied. Nevertheless, a restricted quantity of research has methodically investigated the impact of various inoculum on the initiation phase and overall efficacy of MFCs. The anode's composition and design have a significant impact on microbial adherence, electron transfer, and, in certain instances, direct substrate oxidation. Carbon-based materials, including carbon cloth and graphite felt, are extensively used as anodes owing to their superior electrical conductivity, remarkable durability in microbiological conditions, and substantial surface area that facilitates vigorous biofilm development.

1.3.1. Direct Electron Transfer Pathway

When the electrode material and the cell come into direct physical contact, direct electron transfer (DET) takes place [135]. DET may involve pili-nanowires made by exoelectrogenic bacteria or membrane-bound cytochrome c (cyt c). One benefit of DET has been emphasized by recent research, which indicates that this mechanism is more flexible when it comes to variations in organic load levels or the presence of pollutants [136]. Electrons are transported from the biofilm to the anode surface by conductive tails, often referred to as nanowires or pili,

across distances of up to 10 μm . Research has demonstrated that *Shewanella oneidensis* and *Geobacter sulfurreducens* improve their electron transfer abilities by using nanowires [137]. These microbes create conductive protein filaments, also known as pili or nanowires, which act as electrical conduits for extracellular electron transfer between the material surface and the cell [138]. Moreover, Wang et al.[139] have found that conducting an electric field or altering the pH of nanowires might enhance their conductivity characteristics. According to earlier research, the usage of nanowires by *Geobacter sulfurreducens* [140][141], [142], and *Shewanella oneidensis* improves their capacity for electron transfer. These microbes create conductive protein filaments, also known as pili or nanowires, which connect the material surfaces to the cells electrically and allow extracellular electron transfer [143], [144].

1.3.2. Indirect Electron Transfer Pathway

Redox intermediary variables, whether metabolites generated by the same microorganisms or an exogenous factor, soluble artificial redox mediators introduced into the system, promote indirect transmission. Specific impurities in the medium may potentially serve as electron mediators [145]. Electron mediators enable the transfer of electrons between a microorganism and an external donor or acceptor. Reversible electron transfer mechanisms, robust stability in both oxidised and reduced states, solubility, high negative potential, facile translocation across the bacterial membrane, and extended operational lifespan are essential for mediators to function well. Phenothiazine is synthesised by *Pseudomonas aeruginosa*. [146] thionine Quinones, humic acids generated by *Lactococcus lactis*, and flavins produced by *S. oneidensis* are many instances of facilitated electron transfer.

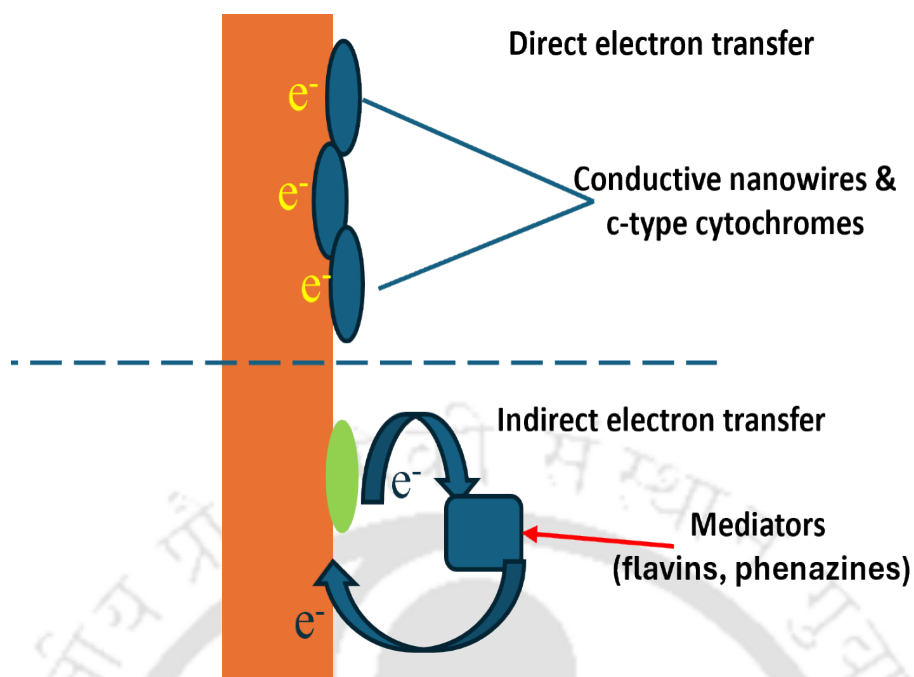


Figure 1.5. Schematic representation of microbial electron transport

1.3.3. Effect of eco-friendly feedstock on the Extracellular Electron transfer route

Various feedstocks significantly influence the characteristics of biochar, including yield, ash content, functional groups, elemental composition, porosity, aromaticity, and specific surface area, as shown by previous research [147]. Surface attributes, including usable size, surface area, and density, can be significantly enhanced by adjusting feedstocks, preparation methods, and modification processes [148]. Comparing the characteristics of biochar produced from diverse feedstocks forms the foundation for the preferential use of biochar to remove a variety of pollutants. The surface of the available bio-based feedstock is essential to functional operations, and its properties can have a big influence on how well it works. In addition to features that are frequently mentioned, including porosity, specific surface area, and functional groups, another significant aspect that affects the efficiency of the feedstock is its surface charge. The surface charge may vary depending on the feedstock solution's pH [149]. Table 1.2

shows the types of electron transfer mechanisms through different PEM MFCs.

1.3.4. Application of Biochar as feedstock in MFC system

The predominant feedstocks used in biochar production are organic waste, wood, and vegetation. Woody biochar has a higher lignin content than herbal biochar, resulting in enhanced thermal stability. Conversely, Ji et al. (2022) indicate that the cellulose and lignin inside herbal charcoal decompose into smaller molecules [150]. Moreover, in comparison to herbal biochar, woody biochar has a greater specific surface area and electron-transfer capacity, enhancing electron production and transfer (Qin et al., 2020b) [151]. The typical temperature to produce wood-based biochar is 1000 °C, significantly above the 500 °C necessary for the creation of cellulosic biochar. Moreover, biochar removed several contaminants from aqueous solutions [152]. Numerous studies indicate that biochar may adsorb organic and inorganic contaminants from wastewater [124]. The physicochemical characteristics of water contaminants and the properties of the biochar itself dictate the efficiency of pollutant adsorption. Biochar has shown efficacy in soil restoration, mostly owing to its ability to absorb organic contaminants and heavy metals from polluted soils [153]. Besides its adsorptive properties, biochar also indirectly affects the makeup and activity of soil microbial communities in the presence of these pollutants [154]. In the early phases of biochar application, a decline in bacterial populations is often seen owing to microbial succession, whereby early-stage microorganisms swiftly exhaust available nutrients, thereby restricting the proliferation of subsequent microbial species [155]. As environmental circumstances stabilize and biochar progressively alleviates metal toxicity, microbial diversity and abundance generally recover and may even increase over time [156]. Recent advancements in sustainable microbial fuel cell (MFC) technology have investigated the use of environmentally benign, bio-based feedstocks. Hemalatha et al. used deoiled *Azolla pinnata* biomass (DAB) for anode manufacturing and substrate production [157]. The DAB was first subjected to pyrolysis to

generate charcoal, which was used as the anode material. Concurrently, the hydrolysis of biomass produced reducing sugars that functioned as the substrate for the MFC. This device demonstrated a 65.6% decrease in chemical oxygen demand (COD) and attained a maximum power density of 105 mW/ m² during testing [158]. The augmentation of extracellular electron transfer (EET) was ascribed to the enhanced activity of complex IV cytochrome c pairs, cytochrome Cox (Cyt Cox) and cytochrome Crd (Cyt Crd). The use of Azolla-derived biochar enhanced bioelectrogenic activity at the anode surface while reducing electron losses, illustrating its dual role as a conductive material and a sustainable bioresource.

1.3.5. Mechanism of Electron transfer via feedstock

Zhang et al. (2023) identify three main processes for electron transfer in biochar-assisted systems: biochar-mediated electron shuttling, direct electron transfer via carbon matrices, and microbial electron transfer [159]. Yang et al. (2020b) previously revealed that Fe (III) and *Shewanella oneidensis* MR-1 cells preferentially aggregate on diminutive biochar particles, therefore augmenting electron shuttling efficiency [160]. The facilitation was ascribed to the presence of semiquinone functional groups on the biochar surface, which serve as efficient redox mediators [161]. Both endogenous and exogenous chemicals, including humic substances and anthraquinone-2,6-disulfonate (AQDS), have shown the ability to act as electron shuttles, enhancing extracellular electron transfer (EET) [162]. The introduction of biochar into microbial systems might enhance the production of extracellular polymeric substances (EPS), such as proteins, polysaccharides, and nucleic acids (Gloag et al., 2021) [163]. Moreover, biochar may improve microbial aggregation and the development of hydrophobic groups by facilitating EPS production [164]. It enhances microbiological viability by adsorbing harmful chemicals, including antibiotics, heavy metals, and ammonium, while releasing critical metal ions necessary for microbial development (Tang et al., 2022) [165]. The electrochemical activity of EPS, often including redox-active constituents, is augmented in the presence of biochar.

These EPS components may function as mediators, enabling electron transfer between bacteria and charcoal particles. Redox-active compounds participating in the processes include flavin proteins, c-type cytochromes, and humic substance analogs, all of which substantially enhance the overall efficacy of electron transfer in biochar-based microbial systems [166].



Table 1.2 Bioelectrochemical reaction with predicted electron transfer mechanisms

Candidate microorganism	Active site	Predicted electron transfer protein	Reaction condition	Application	Byproduct	Reference
Nitrifying Bacteria	Periplasmic space	Flavoproteins	-500 mV vs Ag/AgCl	Direct electron transfer	Nitrate reduction	[167]
<i>G. sulfurreducens</i>	Heme Protein	Cytochrome c	-600mV ag/Agcl	Direct electron transfer	Cr ⁶⁺ Cr ³⁺	[168]
<i>Shewanella oneidensis</i>	Heme protein	Cytochrome c	-600mV Ag/AgCl	Direct electron transfer	Cr ⁶⁺ Cr ³⁺	[169]
<i>Desulfovibrio</i> sp	e-S protein without acid-labile sulfur	Rubredoxin	-700 mV vs. SHE	Indirect electron transfer	Hydrogen production	[170]
Methanogenic bacteria	[NiFe] or [FeFe] or [Fe]-only	Hydrogenase	-550 mV vs. NHE	Indirect electron transfer	Methane production	[171]
<i>Acetobacter pasteurianus</i>	Cytoplasmic membrane	Cytochrome	-590 mV vs. SHE	Electro fuel from CO ₂ and electricity	Acetate	[172]
<i>Shewanella oneidensis</i> MR-1 (nano - nano-nano-	In situ polypyrrole / polydopami	Flavin and outer membrane cytochrome	-	Hybrid DET and MET	5 times increased current, lower R _{ct}	[173]

encapsulated)	ne shell interfaces						
Mixed consortia degrading chlorophenols <i>Pseudomonas aeruginosa</i>	Aryl amines serving as redox mediators	2,4-DCP	Closed-circuit voltage	MET via the consenting community electron shuttles	Degraded intermediates, acetate, lower toxicity	[174]	
	Pyocyanin, phenazine redoxdyes	phenazine compounds		Mediated electron transfer	Carbon dioxide	[174]	
<i>Geobacter sulfurreducens</i>	OmcS/OmcZ(multi-heme c-cytochrome	Cytochrome	Anaerobic	Direct electron transfer	Carbon dioxide	[175]	

1.4. The Linear Economy vs. Circular Economy in Resource Utilization

Diverse environmental contaminants, including endocrine-disrupting chemicals, pharmaceuticals, personal care products, and other hazardous substances, have been detected in the majority of wastewater treatment plants, posing a significant threat to water quality. The conventional linear economy adheres to a “take–make–dispose” paradigm, whereby resources are extracted, converted into goods, and discarded after consumption. This method exhausts limited resources, utilizes substantial energy, and produces considerable CO₂ emissions. Alarming, around 68% of input raw materials are non-renewable, with many being burnt or otherwise disposed of, resulting in significant environmental repercussions [134]. Conversely, the **circular economy** aims to optimise the use of limited resources by facilitating the shift to renewable inputs, prolonging product lifespans, and allowing material recovery post-consumption. The objective is to restore all types of capital, natural, human, social, and financial, while minimising waste production. In this context, **natural biomass** is essential to the developing bioeconomy, facilitating environmentally friendly processes, sustainable resource cycles, and improved interactions between human activities and ecological systems.

1.4.1. Recent Advancements in Microbial Fuel Cell Technology

MFC technology has not been extensively adopted for practical waste treatment applications, mostly due to its nascent stage of development and the need for further time for technological progress. Moreover, its process efficiency is often seen as inferior to that of proven alternatives, such as methanogenic anaerobic digesters. A significant obstacle exists in the design and construction of large-scale, high-performance MFC reactors, impeding their

scalability and wider use. MFC reactors, regardless of being single- or double-chamber systems, produce energy by the microbial oxidation of organic materials. Depict the essential configurations of these reactors and their corresponding electrochemical mechanisms. In both arrangements, electrons generated by microbial activity are collected at the anode and conveyed to the cathode, propelled by the potential difference between the electrodes. At the cathode, electrons engage in reduction processes, while protons liberated at the anode and conveyed to the cathode by diffusion are concurrently used, thus completing the electrical circuit. In double-chamber MFCs, the anode and cathode compartments are divided by a proton exchange membrane (PEM) to sustain a potential difference between them. The anode chamber, operating under anaerobic conditions, accepts organic substrates as the fuel source, while the cathode chamber is supplied with oxygen or an alternative oxidizing agent, such as ferricyanide, to enable cathodic reduction processes. A more efficient and cost-effective structure for generating electricity from the microbial decomposition of organic materials, representing a simplified version of the single-chamber microbial fuel cell (SCMFC). The anode and cathode of a single-chamber microbial fuel cell (SCMFC) are often contained inside the same chamber, either without a separator or with a rudimentary separator. This design significantly decreases internal resistance, manufacturing complexity, and expense. Electrogenic bacteria inhabit the anode surface and initiate the oxidation of organic molecules in an anaerobic environment inside the wastewater or organic substrate of a solid-state methane fuel cell (SCMFC). An electric current is generated at the anode when microorganisms decompose organic materials, producing electrons that are then sent to the cathode via an external circuit. Protons traverse the PEM or electrolyte to the cathode, where they combine with oxygen and electrons to produce water or other benign byproducts. The dual-chamber design enhances the operating efficiency of the MFC, making it suitable for environmental monitoring, wastewater treatment, and renewable energy generation. Carbon

paper, graphite fibre brushes, copper, stainless steel mesh, graphite, and carbon cloth are often used as constituents of electrodes. In tubular MFCs, bigger configurations often have a tubular anode that is electrically isolated from the cathode by a separator. The kind of cylindrical material used, including polyvinyl chloride and tube-formed cation exchange membranes, often dictates the tubular shape [176]. A tubular microbial fuel cell was designed to enhance configuration and scalability for sustainable energy generation. **Figure 1.6** depicts the innovative and compact bioelectrochemical fuel cell, where the tubular structure is cylindrical or coaxial, with electrodes and other components on its surface, oriented along the tube's longitudinal axis. The presence of wastewater along the tubular anode facilitates the development of electroactive biofilms.

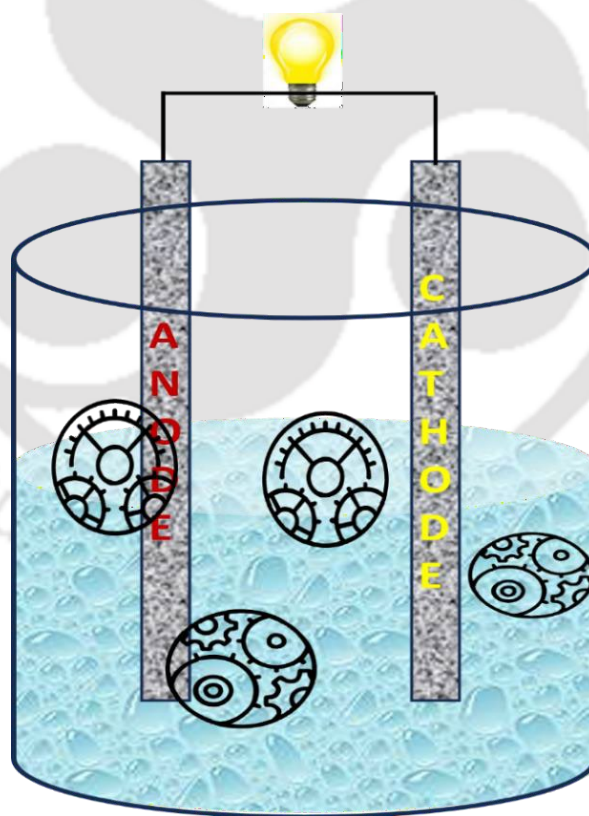


Figure 1.6. Tubular microbial fuel cell reactor

1.4.2. Biomimetic Membrane

The fabrication of separation membranes using biomimetic techniques has seen a rise in attention in recent years. These membranes are either biologically inspired or incorporate biological ideas, concepts, or components. An increasing number of reviews examining various aspects of this field have been published because of the expanding interest in biomimetic membranes across several disciplines [177]. Meier and colleagues' evaluations have covered a lot of ground when it comes to block copolymer (BCP) biomimetic membranes [178]. The performance of conventional reverse osmosis membranes is surpassed by integrating Aqueous Carbonic Anhydrase (AWCs) into scalable biomimetic membranes. This new method improves our basic understanding of how to best incorporate AWCs within their smallest colloidal self-assembled superstructures, which will enable chosen water transport that mostly occurs through channels [179]. These investigations demonstrate how biomimetic and hybrid composite membranes may overcome the drawbacks of conventional MFC components, opening the door to more effective and environmentally friendly energy production systems.

1.4.3. Smart membrane

The past ten years have seen a sharp increase in the development of advanced membranes to improve features including resistance to fouling, enhanced selectivity, and adjustable permeability. Smart membranes have unique qualities, including self-cleaning and anti-fouling, and they are made of materials that respond to stimuli [180]. They have surface wettability that, in reaction to outside stimuli, can alternate between hydrophobicity and hydrophilicity, and vice versa. Notable physical stimuli include light, electricity, magnetism, and temperature. On the other hand, chemical stimuli include modifications to solvent composition, pH, and ion concentration. The capacity to self-sufficiently customize pore size and surface properties employing temperature gradients, light exposure, alterations in pH, magnetic or electric fields, and certain ions or molecules has led to the development of smart gating membranes for water

treatment, which are inspired by stimuli-responsive cell channels [181]. Membranes, fabrics, and foams are among the materials that have been thoroughly reviewed and contrasted in several evaluations that feature switchable wettability. Upon external stimulation, these materials can experience a full and reversible change in surface wettability. Nevertheless, few papers provide a thorough summary of the stimulus-response behaviour of smart membranes [182]. The addition of smart substances to these membranes' surfaces allows them to respond to external signals by modulating the micro-morphology and energy at the membrane's surface, changing the membranes' surface properties [183]. In the field of oil/water separation technologies, two main categories of materials have been recognized and applied: absorbent materials, which include gel, powder/particle, and nanocomposite, and filtering elements consisting of film, membrane, mesh, and filter [184]. However, the production and use of ceramic membranes obtained from waste presents some difficulties. The first challenge in guaranteeing homogeneous structures and characteristics for the produced membranes is the variety of compositions and contaminants present in waste materials from various sources and processing techniques. This might lead to problems with quality control [185]. A hybrid smart membrane (Figure 7) has been created by Pantuso et al. by the combination of porous PVDF and a thin layer of PVA hydrogel with thermosensitive TS crystals, which is a stimuli-responsive organic crystal showing mechanical motion or structural changes in response to stimuli such as temperature. that are oriented and distributed randomly. This novel membrane combines self-cleaning properties with stimuli-responsive organic crystals for intelligent separation. By reducing fouling, this design seeks to increase effectiveness and prolong operating longevity. The technique presented here paves the way for the development of versatile, energy-efficient hybrid membranes that may be used in a variety of separation procedures, including water desalination.

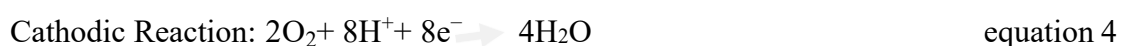
1.4.4. Real-time data sensing and bioenergy production in MFC

Leveraging the use of the biological energy that microorganisms create during the metabolism of organic substrates is used by microbial fuel cells (MFCs) to produce power. Protons and electrons created during the breakdown of organic materials are transported through an external circuit and PEM, respectively, to the cathode. Electrons with high energy are released during the metabolic pathway's breakdown of organic molecules. When oxygen isn't present, these electrons migrate toward the cathode, where they generate electricity. As more substrates are oxidized by microorganisms in the MFC's anodic chamber, Oxidation produces carbon dioxide as a byproduct. However, because the process is derived from renewable biomass, there is no net rise in carbon as a result of it. Furthermore, residential sewage and organic wastewater may be converted by microorganisms in the MFC into electricity [186]. Electrons are conducted by an external circuit to the anodic chamber to produce electricity; meanwhile, protons diffuse through the PEM to the cathodic chamber, where they mix with oxygen to generate molecules of water. In this dissimilative process, microorganisms inside an anodic compartment absorb the protons and electrons from organic substrates. According to its theory of operation, MFC uses microorganisms' metabolic power to biodegrade organic substrates and produce energy by moving electrons entering the circuit from the cell. Without oxygen, microorganisms break down organic substrates in the anodic chamber to produce protons and electrons. Electrons are subsequently transmitted to terminal electron acceptors, including oxygen, nitrate and ferric ion, through the electron transport chain. Alternatively, the electrons can be used for electron shuttling to the anode whenever an electron acceptor is absent. The anode functions as the end of the electronacceptor in mediator-less MFCs, and anodophiles build a biofilm during anaerobic metabolism. Within mediated electron transfer, microorganisms employ a biological method to get exogenous mediators (dyes or metalorganic) or native redox chemicals (quinones and flavins)to transfer electrons across the terminal and anode surface respiratory enzymes [149].

When it comes to producing energy from organic matter, using MFCs has several benefits over other approaches [150].

- i. **High Conversion Efficiency:** Electric energy production involves the efficient conversion of substrate energy, leading to increased output.
- ii. **Ambient Operational Requirement:** MFCs can function by differentiating them from the existing bio-energy processes at room temperature, and even at low temperatures [187]
- iii. **Organic matter type and concentration:** It directly influences the MFC's ability to produce electrons and its overall energy output when it comes to organic materials.
- iv. **Minimal waste treatment:** MFCs release off-gases with a high carbon dioxide concentration and no additional harmful residues, eliminating the need for extensive waste treatment of gases.
- v. **Impact of External Load Limit:** The MFC's external resistance is crucial in determining the output of power and current, requiring a careful balance of power density and system stability.
- vi. **Charge separator:** Positioned makes it easier for protons to go from the anode to the cathode between the two chambers.
- vii. **Self-aeration:** MFCs don't require a separate aeration facility, as the cathode itself can provide a self-aeration facility.
- viii. **Versatility in Industrial Application:** MFCs find wide applications in industries relying on electrical instruments and appliances, particularly in fuel cells, contributing to their success.

Electrode Reactions in MFCs Using Different Substrates



Two chambers - a cathodic chamber and an anodic chamber make up the optimal MFC arrangement. Glass, Plexiglas, or polycarbonate make up the walls of the chambers. Frequently utilized electrodes include graphite, reticulated vitreous carbon, platinum black, graphite fabric, and carbon cloth. A membrane for proton exchange (PEM) divides these chambers from one another. Within the anodic chambers, microorganisms break down the organic substrate to produce protons and electrons, which in turn provide energy and allow for development. The circuit is completed by the cathodic chamber, which is filled with a high-potential electron acceptor solution. This type of arrangement is used extensively because of its effective energy recovery with minimal negative impact on system performance and stability [188]. One often utilized harmless electron acceptor is oxygen. As a replacement, power density may be maximized using conventional media, including ferricyanide. There are two MFC system designs that are commonly used, while certain prototype models include changes. The capacity of some species, such as *Shewanella* and *Geobacter*, to transmit electrons effectively is what propels the transformation of organic materials into useful power. These microorganisms take part in direct and mediated electron transfer routes, which are two types of electron transfer processes found in the MFC, and both increase the overall efficiency of energy conversion. Additionally, MFCs include charge separators, including microbial films or proton exchange membranes, which are essential for preserving the electrochemical gradient and raising power production in a variety of MFC designs. Through the utilization of various microorganisms and the enhancement of electron transfer mechanisms and charge separators, MFCs provide a viable path towards the generation of bioenergy that is sustainable.

1.4.5. Energy Recovery Mechanisms in Microbial Fuel Cells

Traditionally, microbial fuel cells use microorganisms as biocatalysts to produce power from waste and wastewater originating from home, industrial, agricultural, and other sources. [189].

The literature mostly reports uses of MFCs in energy production and wastewater treatment.

Additionally, MFCs have been used for monitoring wastewater quality and treating various waste streams, such as sludge, salty water, purified terephthalic acid, industrial effluents, urine, abattoir wastewater, animal waste, and petrochemical discharges. [190]. The direct electron transfer (DET) process depends on the ability of electroactive bacteria, or exoelectrogens, to transport electrons directly to conductive anode materials via anodic respiration, eliminating the need for additional mediators. A thorough understanding of microbial interactions enhances the optimisation of operational parameters to achieve maximum power density and cost-effective performance. Although a lot of research is done in lab settings, real-world circumstances are very different. Small, treated water volumes, a single pollutant selection, and minimal thought given to equipment location or ease of repair are some of the disadvantages of laboratory treatments. Reactor arrangement, as well as material of the electrode, substrates type, pre-treatment, microbial population, substrate operating phase, organic loading rate (OLR), and operational parameters, are some of the variables that affect how well-complicated waste is treated in microbial fuel cells (MFCs). Comparing studies is difficult even with a wealth of MFC research because of variations in substrate materials, reactor configurations, data collecting techniques, experimental design specifications, and inconsistent performance metrics [191]. Membrane-less microbial fuel cells (MFCs) use electrolytes serving as a partition between the anode and the cathode, using either a non-selective separator or no membrane at all. Three important aspects of separator materials are low cost, long lifespan, and strong mechanical properties. Any material in the substrate can be transmitted to the cathode by these non-selective separators, increasing the quantity of oxygen that diffuses into the anode chamber. Because of aerobic substrate digestion, membrane-less reactors often have lower coulombic efficiency than MFCs with selective membranes. The most economical option would be membrane-less MFCs if the problem of low coulombic efficiency could be solved.

1.5. Refining membrane technologies for substrate separation and energy retrieval in MFCs

The membrane physically separates the electron acceptor chamber from the anaerobic anode in a microbial fuel cell (MFC) device that generates bioelectricity [131]. Eight percent of the total expenditure is ascribed to catalysts and membranes. No membrane has been developed for dual-chamber MFCs, despite the need of separators in these systems. A multitude of researchers have addressed this issue, as detailed in the following sections. The efficacy and overall expenses of MFC systems are significantly influenced by membranes; hence, to substitute expensive materials with more economical alternatives, it is essential to possess a thorough understanding of membrane kinds. Moreover, membranes influence internal resistance; membranes with high resistance correlate with suboptimal performance since they hinder proton transport and ion exchange, thus leading to diminished current and power densities [192]. Controlling biofouling is a significant challenge in several applications, such as membrane systems, detection systems, medicinal operations, and water treatment. Biofouling refers to the accumulation of invasive organisms, including bacteria (such as *E. Coli*), algal spores, unicellular eukaryotes, and multicellular animal larvae. The colonisation results in the formation of densely bonded biofilm cells, which may disrupt the aforementioned processes. **Figure 1.7** depicts several categories of membrane-based microbial fuel cells (MFCs) for data recording and performance matrix analysis. Every MFC design has distinct characteristics and problems, highlighting the need of thorough consideration for optimal use.

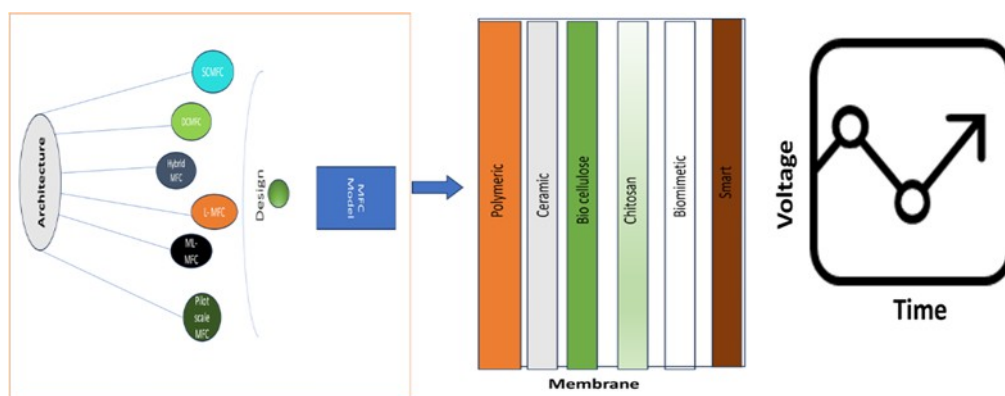


Figure 1.7. Schematic representation of microbial fuel cell (MFC) architectures and membrane material classifications for energy generation

1.5.1. Fueling Microbial power through biomass optimization

Microbial fuel cells (MFCs) are apparatuses that use diverse organic substrates to generate bioelectricity. Additionally, various types of wastewater, such as metal-contaminated, mining-related, domestic, municipal, agricultural, swine, textile, paper mill, brewery, and distillery effluents, as well as marine sediments, have been utilised in MFC systems to generate bioelectricity. Researchers have shown that bacteria may transmit electrons (e^-) to conductive materials via surface contact by using a mix of exoelectrogenic and endoelectrogenic mechanisms. The substrate used significantly influences the performance of microbial fuel cells (MFCs). Basic substrates readily used by exoelectrogenic bacteria, such as acetate and glucose, often provide higher power densities [133]. Complex substrates with diverse power densities, such as wastewater from residential and commercial sources, provide significant potential when subjected to appropriate microbial acclimation and pre-treatment. Industrial wastewater sometimes poses additional challenges due to inhibitory substances; yet, it may still be advantageous with the proper microbial consortia. The enzymatic degradation of biopolymers like starch and cellulose is essential for their utilisation, which may reduce power density but has considerable energy yield potential when supported by appropriate microbial populations.

Table 1.3 presents the variety of Exoelectrogenic and Endoelectrogenic microbial performance in MFCs. This comparative study facilitates the understanding of the potential energy output yield of microbial fuel cells (MFCs) using diverse substrates, especially complex wastewater substrates. By understanding the performance characteristics of both endoelectrogenic and exoelectrogenic bacteria on various substrates, researchers may more precisely predict and enhance MFC efficiency for practical applications. The total efficiency of the MFC system is enhanced by electro-fermentation microorganisms that facilitate electron transmission between microbial cells and electrodes. Electro-fermentation enhances the efficacy of MFC systems by augmenting power generation, boosting the production of vital fermentation products, and improving wastewater treatment efficiency. The integration of electroactive microorganisms into microbial fuel cells (MFCs) might lead to substantial advancements in technologies about sustainable energy and environmental conservation. Future studies should focus on enhancing microbial populations, electrode materials, and operational parameters to fully realise the potential of electro-fermentation in MFC applications.

Table 1.3. Comparative study of basic Substrates in the MFC system

MFC type	Microbial consortium	External mediator	Substrate type	Electrode	Buffer solution	Optimum power density (mW/m ²)	Reference
NA	<i>Desulfovibrio alaskensis</i> G20	Transmembrane complexes, tetraheme cytochrome C3	Sodium lactate	NA	MO Basal salt	NA	[193]
Three compartments	<i>Acetobacter aceti</i> <i>Escherichia coli</i> strain K-12	NA	Cattle wastes	Graphite fiber brush	NA	216	[194]
Double chambered	NA	riboflavin and anthraquinone-2-sulphonate, AQS	Anaerobic sludge	Carbon felt/O ₂	PBS 100 mM	1.06	[195]
Single chambered	NA	NA	Wastewater & MFC effluent	Stainless mesh/O ₂	PBS ~86 mM	NA	[196]
Single-chambered air cathode	<i>Acinetobacter</i> Mixed bacterial culture	NA	L-Glutamic Acid	Carbon cloth	NA	686	[197]
Two-chamber MFC	Fungal growth medium	NA	Naphthalene	Graphite plate	50 mM of phosphate buffer	132	[198]
Double chambered	<i>Klebsiella pneumoniae</i> – FA2	NA	Food industry wastewater	Graphite plate	Phosphate buffer	428	[199]
Dual chamber MFC	<i>Serratia marcescens</i> AATB1	Lumiflavine	Septic tank wastewater	Graphite plate	50mM phosphate buffer	341	[200]

1.5.2. Real wastewater as substrate

The use of microbial fuel cells (MFCs) has been the subject of much research. Numerous studies have examined the energy conversion efficiency of microbial fuel cells (MFCs) using four unique substrates: lactate, glucose, acetate, and propionate. MFC systems using methanol and ethanol as substrates, with ethanol achieving a 10% elimination efficiency, have a maximum power density of 488 mW/m². A variety of wastewaters have been examined for power generation in microbial fuel cell (MFC) systems, including swine wastewater, aquaculture effluent, tannery discharge, landfill leachate, food manufacturing wastewater, domestic wastewater, and agricultural and livestock wastewater. In MFCs, a single group used six distinct carbon sources: glucose, maltose, sucrose, lactose, galactose, and mannose, with *Proteus vulgaris* functioning as the biocatalyst. A recent study indicates that lignocellulosic biomass carbohydrates might serve as a valuable feedstock for power production in microbial fuel cell (MFC) systems. Robust wastewater has been examined as a viable substrate for generating energy in microbial fuel cells. Examples of this wastewater include swine and animal carcass effluent. Single-chambered MFC systems have been shown to provide superior power outputs compared to dual-chambered systems while using swine wastewater [201]. Furthermore, an array of food wastes has been assessed for their potential to generate bioelectricity in MFC systems; these include composite food waste and mixed veggies, and compound food waste from canteens. Dairy wastewater has been studied for bioelectricity production in MFCs, obtaining notable power densities and COD removal efficiency. Dairy wastewater is recognized for its high content of fermentative organic biodegradable matter. In addition to their improved conversion efficiency and decreased solid waste output, microbial fuel cells (MFCs) provide several benefits over traditional wastewater treatment systems. One of the main advantages is that they can function in a variety of climatic settings since they can run at room temperature. Research indicates that MFCs may eliminate all pollutants, including

chemical oxygen demand (COD), from wastewater and produce power densities as high as 4200 mW/m^3 [201]. It has been demonstrated that a wide variety of bacterial communities, both in mixed and pure cultures, can oxidize organic molecules in wastewater and transport electrons to the anode, which helps to facilitate this process. Notwithstanding these encouraging characteristics, inappropriate waste management practices persist in contaminating the ecosystem, underscoring the necessity for efficient treatment methods. Although wastewater treatment units have difficulties turning waste into goods with added value, modular fuel cells (MFCs) have shown promise in treating wastewater and producing electricity, especially in isolated locations. Though high-power output is still a technically difficult problem that must be resolved for market readiness, the commercialization of MFC technology is still in its early stages.

1.5.3. Metrics of Assessing MFC Performance

Despite extensive research conducted in laboratory environments, real-world conditions significantly differ. Limitations of laboratory treatments include small volumes of treated water, selection of a single pollutant, and insufficient consideration of equipment placement or maintenance accessibility. Factors influencing the efficacy of complex waste treatment in microbial fuel cells (MFCs) encompass reactor configuration, electrode material, substrate type, pre-treatment processes, microbial populations, substrate operational phases, organic loading rates (OLR), and operational parameters. The comparison of studies is challenging, even with a substantial body of MFC research, due to discrepancies in substrate materials, reactor designs, data collection methodologies, experimental design criteria, and inconsistent performance metrics [202]. Membrane-less microbial fuel cells (MFCs) use electrolytes as a barrier between the anode and cathode, using either a non-selective separator or the absence of a membrane entirely. Three critical characteristics of separator materials are affordability, durability, and robust mechanical qualities. These non-selective separators may transfer any

substance in the substrate to the cathode, hence augmenting the amount of oxygen that diffuses into the anode chamber. Due to aerobic substrate digestion, membrane-less reactors often exhibit reduced coulombic efficiency compared to MFCs with selective membranes. The most cost-effective solution would be membrane-less MFCs, provided the issue of poor coulombic efficiency is addressed. Coulombic efficiency is defined as the ratio of the electrons recovered as electrical current to the total electrons theoretically obtained through substrate oxidation. In MFC, coulombic efficiency is calculated as the ratio of total coulombs measured by integrating current over time to the theoretical coulombs available based on substrate removal (typically expressed through COD) [5], [6]. The formula for calculating Coulombic efficiency is as follows:

$$CE (\%) = M \int_0^t \frac{I dt}{F b V_{an} \Delta COD_x} \times 100$$

Where M is the molecular weight of oxygen, I represents current, dt is the time interval, F is Faraday's constant, and b is the number of electrons exchanged per mole of oxygen (4 mol e⁻/mol O₂). The table of a microbial fuel cell is Table 1.4. provides a detailed examination of MFC performance across several configurations, each exhibiting differing power densities. Dual-chamber and stacked configurations often provide greater power outputs compared to single-chamber and membrane-less alternatives. Microfluidic MFCs and hybrid systems provide considerable promise due to their innovative features and high efficiency. Enhancing the efficiency and scalability of MFCs for practical applications requires continuous optimisation and the incorporation of novel materials and technologies

Table 1. 4. Comparative analysis of power density with different MFC configurations

Sl. no	MFC configuration	Substrate type	Bacterial species	Working volume (L)	Membrane	Power density (mW)	Reference
1	Upflow membrane less	Domestic wastewater	<i>Geobacter metallireducens</i>	0.85	Nafion™117	40	[203]
2.	Two chambered	Diary wastewater	NA	2	Nafion 117	621	[204]
3.	Two-chambered loop	Piggery wastewater	NA	1	CMI-7000	1415	[205]
4.	Membrane less	Sewage wastewater	Mixed culture	0.11	gravel	6.73	[206]
5.	Tube MFC	Soil sample mixed effluent	<i>Pseudomonas chlororaphis</i> <i>PCL1391</i> <i>Shewanella oneidensis</i> MR-1		NA	NA	[207]
6.	Dual chambered	Synthetic substrate	<i>Lactococcus lactis</i> NBRC12,007	0.4	NA	0.15	[208]
7.	Dual chambered	Yeast extract	<i>Klebsiella pneumoniae</i> AATB2	NA	NA	1143	[209]
8.	Dual chambered	Septic tank wastewater		0.25	Nafion-117	257	[210]
9.	Dual-chambered MFC	Pharmaceutical wastewater sludge	<i>Lysinibacillus sphaericus</i>	0.10	NA	850	[211]
10.	Dual chambered	Acetate, glycerol	<i>Arthrospira maxima</i>	0.10	fluoro-based	100	[212]
11.	Single chambered	Biodiesel wastewater	NA	0.50	NA	487	[213]

1.6. Techno-Economic Analysis of Membrane-Integrated MFCs

This assessment suggests that microbial fuel cells (MFCs) are generally economically beneficial, with an annual running cost usually ranging from €1700 to €2300, much lower than conventional methods. The subsequent expense, however, excludes the need of replacing the electrodes or membranes. Unlike conventional wastewater treatment facilities, the initial cost of MFC technology exceeds the operational expenses, requiring the development of very durable components to enhance the method's economic viability. A brush-type current collector is required for anode electrodes, typically constructed from carbon fibre with embedded graphite, around a corrosion-resistant metal core such as titanium or stainless steel. An alternative is to use stainless steel or tungsten-infused carbon granules. Cathode electrodes typically represent 47–75% of the total cost of a standard MFC. Air cathodes are recommended due to the availability of inexpensive metal mesh current collectors, such as nickel foam or stainless steel, known for their superior conductivity and affordability [215]. It is well-established that proton exchange membranes (PEMs) constitute the majority of the manufacturing cost for microbial fuel cells (MFCs). As seen in Table 1.5. Summarising the prominent trends seen in the latest cost assessments of various membranes used in Microbial Fuel Cells (MFCs). The power-to-cost ratio often remains below 1 mW USD⁻¹, despite Nafion 117 consistently generating elevated power densities. This is attributable to its high price, which significantly diminishes its cost-effectiveness. The commercial proton exchange membrane, Ultrex CMI-7000, composed of polystyrene crosslinked with divinylbenzene, has a power-to-cost ratio of less than 1 mW USD⁻¹, similar to the previously stated membrane. These findings underscore the need to identify novel, cost-effective membrane materials that exhibit electrochemical efficacy. Utilising waste-to-energy (WTE) channels to harness energy from waste streams is seen as a viable strategy for waste management and sustainable energy

generation. Research predicted that the minimum selling price for ethanol derived from food waste (MESP) would be USD 548.48 per tonne (or 19.36 cents per litre) [216] . This is almost fifty percent of the gasoline-ethanol cost, projected to be USD 1082 per tonne in 2022. Evaluating financial metrics such as the Internal Rate of Return (IRR), Discounted Payback Period (DPP), Benefit-Cost Ratio (BCR), and Net Present Value (NPV) to ascertain economic viability. As MFCs are seldom used in microgrids, the increased capital, operational, and maintenance costs of these devices have not been standardised. The corrosive properties of wastewater fumes complicate the estimation of the anticipated long-term usability, since they may rapidly deteriorate metal buildings and need extensive maintenance over an extended period.

1.6.1. Scaling up MFC

Scaling up MFCs is an important step that involves lifecycle evaluation and techno-economic concerns. One noteworthy example of a scale-up is provided by those who used clayware as a separator to create an affordable 26-liter air cathode MFC. They achieved a maximal power output of 17.85 mW and a Coulombic efficiency (CE) of 5.1%, reporting steady performance for as long as fourteen months [217]. They also presented several MFC demos, emphasizing that clayware MFCs with tubular designs may be maintained for four years with little upkeep. Due to automation and the fact that MFCs do not require aeration at wastewater treatment facilities, it has the potential to lower total costs. This estimate indicates that MFCs are often very economically advantageous, with total annual running costs ranging from €1700 to €2300, far less than those of traditional procedures. This cost, however, does not account for the requirement to replace the electrodes or membranes. Building very robust MFC pieces is essential to improving the process's economic feasibility. This is because, in contrast to traditional treatment systems, the cost of capital exceeds the cost of upkeep. This is because, in contrast to traditional treatment systems, the cost of capital exceeds the cost of upkeep. To draw

investors for research and development for commercial applications, **Figure 1.8** presents the techno-economic analysis of microbial fuel cells in the areas of sustainable power production and wastewater treatment. To attract investors, several cost aspects are carefully considered, such as the initial investment, operating expenditures, prospective electricity output, and waste treatment capability. MFCs must be developed at the lowest possible cost to provide conventional carbon-emitting energy sources a competitive advantage.

1.6.2. Optimisation in MFC

The energy efficiency of a microbial fuel cell (MFC) is primarily defined by its capacity to transform the chemical energy contained in organic substrates into usable electrical energy. Achieving high power densities while keeping low operating costs is crucial for these systems to be commercially viable [218]. However, poor energy efficiency remains a chronic issue, frequently restricting practical application. This inefficiency may be attributable to numerous reasons, including high internal resistance, voltage losses owing to methanogenic activity in the anode chamber, electrode polarization, material deterioration, and suboptimal operating circumstances [219]. Furthermore, mass transfer limitations such as limited substrate diffusion, thick biofilm growth, product buildup at the anode, and oxygen crossing at the cathode further decrease system performance. One of the most fundamental obstacles in scaling up MFCs is the dramatic loss in energy efficiency with increasing reactor size. Compared to conventional fuel cells or batteries, MFCs tend to provide lower power outputs. This is mainly due to increasing ohmic resistance, which emerges when the physical dimensions of reactor components grow. In large-scale systems, voltage losses are increased by expanded electrode spacing and higher membrane surface areas, both of which enhance undesired oxygen transport into the anode compartment. Despite these constraints, expanding MFCs from laboratory prototypes to field-deployable units provides enormous socioeconomic and environmental advantages, notably in wastewater treatment applications. Electrically self-sustaining and

compartmentalized MFC units may boost operational stability and efficiency in decentralized treatment systems. However, three primary challenges inhibit commercialization: high system cost, low energy production, and poor end-user acceptability. Among all components, the membrane and electrodes, especially the cathode, constitute the biggest amount of the overall system cost [220]. To solve these issues, the development of cost-effective reactor components and optimum designs is crucial. A potential approach is the use of tubular reactor designs, which provide modular stacking and aid in preserving optimal cross-sectional geometries. A flexible and scalable large-scale MFC architecture may be created by connecting several tubular units in this form, which allows for scalability.

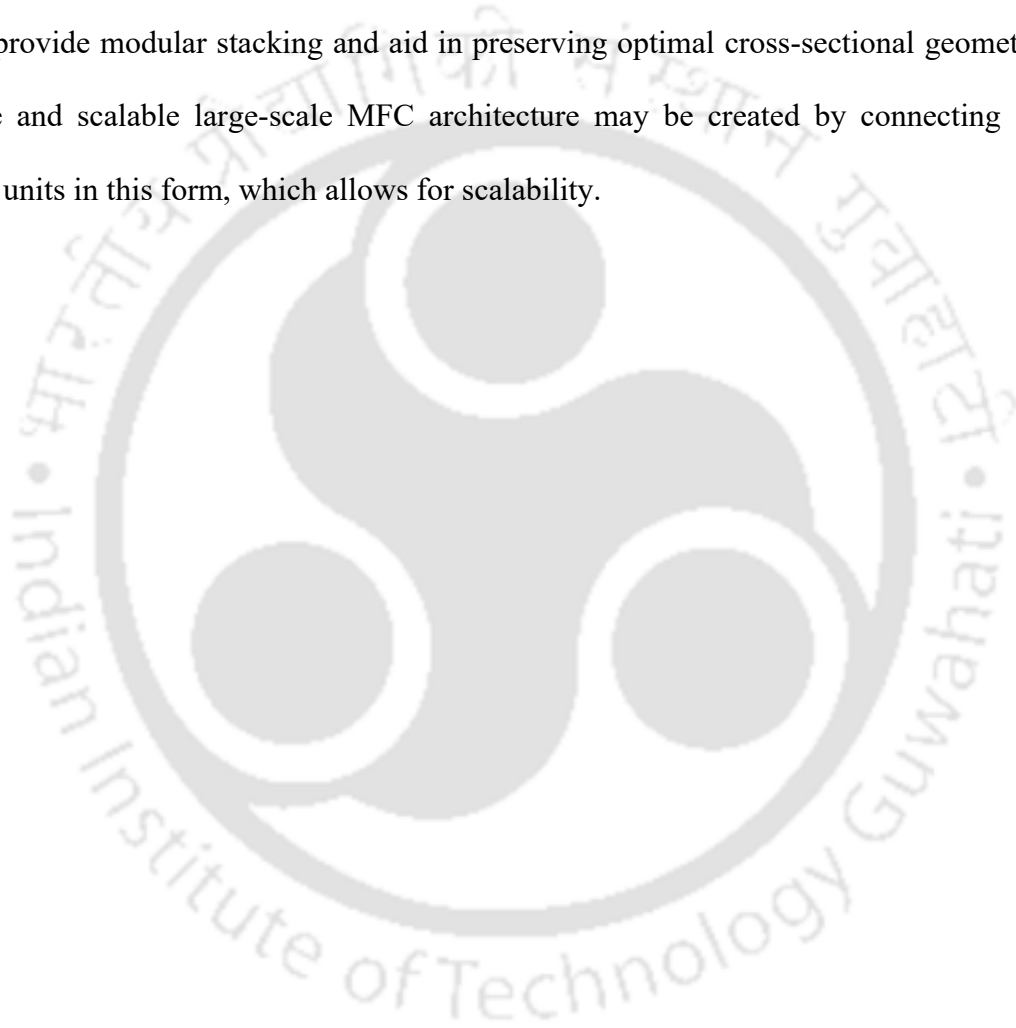


Table 1.5. Comparative cost analysis of the membrane used in microbial fuel cells

Membrane type	Base material	Max power density(mW/m ²)	Time	Experimental condition	Optimization temperature	Cost (mWUSD ⁻¹)	Reference
Porous/biomass-based membrane	Cellulose	117	-	Synthetic wastewater-based DCMFC	30 °C	0.231	[221]
Cationic exchange membrane	SPEEK	226	3	Desalination batch mode MFC	22 °C	1.14	[222]
Biobased membrane	Clay and Goethite combination	112.8	100	Synthetic wastewater-batch mode DCMFC	27 °C	0.186	[223]
Anionic exchange membrane/ cationic exchange	PVDF + cellulose acetate and GO combination	150.2	30	Sucrose solution induced batch mode DCMFC	-	0.316	[224]
Nafion proton exchange membrane	Perfluorosulfonic acid	872	4.17	Sodium acetate substrate induced fed batch DCMFC	20 °C	0.48	[225]
Mullite ceramic membrane	Alumina and silica	15.4	10	Human urine-based continuous SCMFC	-	0.84	[226]
Cationic exchange membrane	Ultrex (CMI 7000) polystyrene crosslinked with divinylbenzene	38.39	-	Fed batch DCMFC	-	0.154	[227]
Anionic membrane	Agar combined with other functional groups	547.4	15	Batch mode SCMFC operated with leachate sanitary landfill	-	39.1	[228]

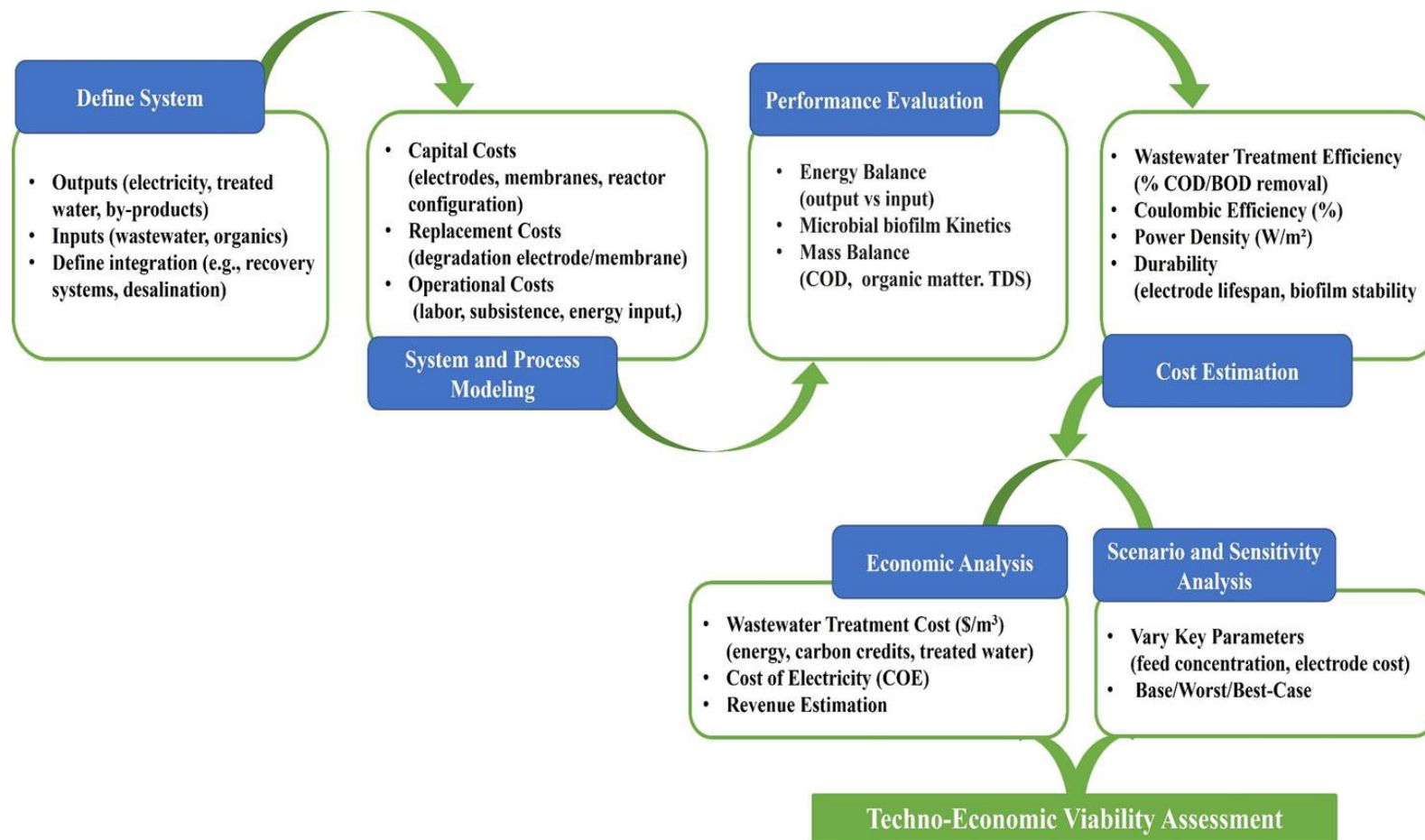


Figure 1.8. The strategy involved in the techno-economic analysis of integrated MFCS

1.7. Research Objectives

Based on the current status of research in the field of practical application of MFC for real wastewater treatment, the following research objectives have been formulated to evaluate the feasibility of employing bio-inspired polymeric membranes as a sustainable alternative to conventional membrane materials.

1. Development of micron-scale MFC and smart data logging system for real-time monitoring of start-up period in wastewater-fed MFCs.
2. Investigation of the role of PFAs-free biopolymer-based proton exchange membrane on the performance of Biomimetic micron-scale MFC.
3. Development of antibacterial composite membrane using green solvent method for energy recovery in hospital wastewater-fed microbial fuel cell.
4. Development of next-generation graphene oxide modified cellulose ether charge separator for antibiotic micropollutant removal and energy recovery in real HWW-fed MFC.

1.7.1. Significance of the work and thesis outline

In the pursuit of sustainable energy solutions, microbial fuel cells (MFCs) have emerged as a promising technology capable of simultaneously generating electricity and treating wastewater. Despite their potential, several scientific and engineering challenges still hinder their large-scale and practical implementation. Therefore, the present study holds significant importance in enhancing MFC performance while reducing overall system cost.

MFCs are inherently bio-electrochemical systems where microbial metabolism, proton transport, and electron transfer occur simultaneously within complex liquid media. To achieve a comprehensive understanding and improvement of system behaviour, the following strategic approaches were adopted: a) experimental investigation using real wastewater in

miniaturised MFC setups, enabling high surface-area-to-volume ratios, faster reaction kinetics, and better control over microbial–electrode interactions; b) development and characterization of biofilms using mixed microbial consortia derived from wastewater; c) real-time monitoring of the MFC start-up and acclimation period using a microcontroller-based smart data logging system; and d) fabrication and modification of membranes for improved proton transport and pollutant removal.

This study is unique due to the design and thorough assessment of a range of bio-based, biodegradable, and ecologically friendly membrane materials, particularly developed for MFC applications. Unlike PFAS-based commercial membranes, which are expensive, chemically demanding, and ecologically enduring, the suggested membranes are composed of natural polymers, providing a sustainable and economical alternative while maintaining electrochemical performance. Chapter One covers a comprehensive introduction to MFC technology, its benefits in wastewater treatment, and the rationale for this study. Chapter Two delineates the experimental procedure, materials, and techniques used. Chapter Three talks about making and improving a small MFC system that is meant to speed up microbial acclimation and improve electron transfer efficiency by increasing the surface-area-to-volume ratio. In addition to developing the reactor, a smart data-logging system based on a microcontroller was designed and added to the reactor. This system allows for continuous real-time monitoring of electrical output during the start-up and stabilisation period, making it a cheaper option than commercial electrochemical monitoring systems. It also explores the implementation of PFAS-free, bio-derived proton exchange membranes within a biomimetic flow channel configuration to address membrane cost, environmental toxicity, and oxygen crossover challenges typically associated with commercial separators. Chapter 4 discusses the fabrication of an antibacterial biopolymer-based composite membrane utilising a green solvent method that is environmentally friendly. It also discusses the use of the membrane in

a microbial fuel cell that operates on hospital wastewater. The chapter talks about how the membrane can stop biofouling while also improving energy recovery and wastewater treatment efficiency. It does this by looking at the membrane's antimicrobial properties, proton conductivity, and electrochemical performance. Chapter five discusses the creation and testing of a graphene oxide (GO)-modified membrane that is meant to improve the removal of the antibiotic ampicillin from wastewater in a microbial fuel cell system and lower the chemical oxygen demand (COD). This chapter looks at the membrane's ability to selectively transport substances, adsorb them, and perform electrochemically, while also looking at its two roles in removing pollutants and generating electricity. The results show that modifying GO greatly increases the efficiency of breaking down pollutants and lowering antibiotic levels. This shows how important it is as a long-lasting and versatile membrane solution for advanced wastewater treatment and controlling antibiotic resistance. In the final chapter, we summarise our conclusion and impact on the research conducted and discuss the way forward in MFC application in future. In addition to this last page includes references, research outputs in the form of papers published and conferences attended so far as part of the research journey.



Chapter 2

Materials and Methods

2.1. Chemicals for membrane and inoculum preparation

The inoculum with mixed culture has been prepared for the MFC module along with the PVA-GA crosslinked charge separator by following the steps mentioned in [229]. The graphite-felt electrode is used in both the anode and cathode chambers. Nafion-117 was used as a control. Sodium acetate (Sigma-Aldrich, St. Louis, MO; Ultrapure water ($18\text{ M}\Omega\cdot\text{cm}$) (purified using a Milli-Q Advantage A10 from Millipore, Billerica, MA) Poly (vinyl alcohol) (Mw 89,000-98,000, 99+ % hydrolysed, density 1.19-1.31 g/cm^3) (Sigma-Aldrich) was used.

2.1.1. Preparation of the membrane

Two types of PVA-based membranes were fabricated using the solution casting technique: a pure PVA membrane and a crosslinked PVA membrane, in which PVA was crosslinked with glutaraldehyde as shown in Figure.2.1. 5%,10%,15%, and 20% PVA powder and distilled water were combined to make PVA solutions. At room temperature, PVA powder was gradually added to distilled water. To get homogeneous solutions, the mixture was agitated for two hours at $90\text{ }^{\circ}\text{C}$. The polyvinyl alcohol used had a degree of polymerisation of 1700 and a saponification level of 98–99%, indicating a high molecular weight and purity. The PVA–GA crosslinked polymer membrane was fabricated via a two-step process. Initially, different concentrations of deionised water were used to dissolve PVA, and subsequently diluted with distilled water under continuous stirring at 620 rpm until fully dissolved. To eliminate all the trapped bubbles, the PVA solution was sonicated for one hour at room temperature before casting. In the polymer solution, a chemical crosslinker amount equal to 50% of the polymer's weight of chemical crosslinker, namely citric acid, glutaraldehyde, and sodium sulphate, was added at $40\text{ }^{\circ}\text{C}$ for 12 hours. The casting procedure was then started after the solution had been left for a further hour [230]. In order to avoid the film from dissolving in the crosslinking solution while the reaction was taking place, sodium sulphate was added to the mixture [231]. After the crosslinking procedure,

the produced membrane was finally rinsed with clean water to get rid of any remaining glutaraldehyde and citric acid, and it was left to dry at room temperature. This solution was then cast onto a Teflon plate, forming a wet membrane with a thickness ranging between 200 and 400 μm as shown on **Figure 2.1**. The casting container was reweighed, and the membrane was allowed to dry at 25 $^{\circ}\text{C}$ under 30% relative humidity, enabling slow evaporation of excess water. Experiments were conducted to determine the developed membrane's swelling and water adsorption of the developed membrane after the membranes had dried. Properties were compared with Nafion 117 as PEM, and all analyses were carried out in triplicate.

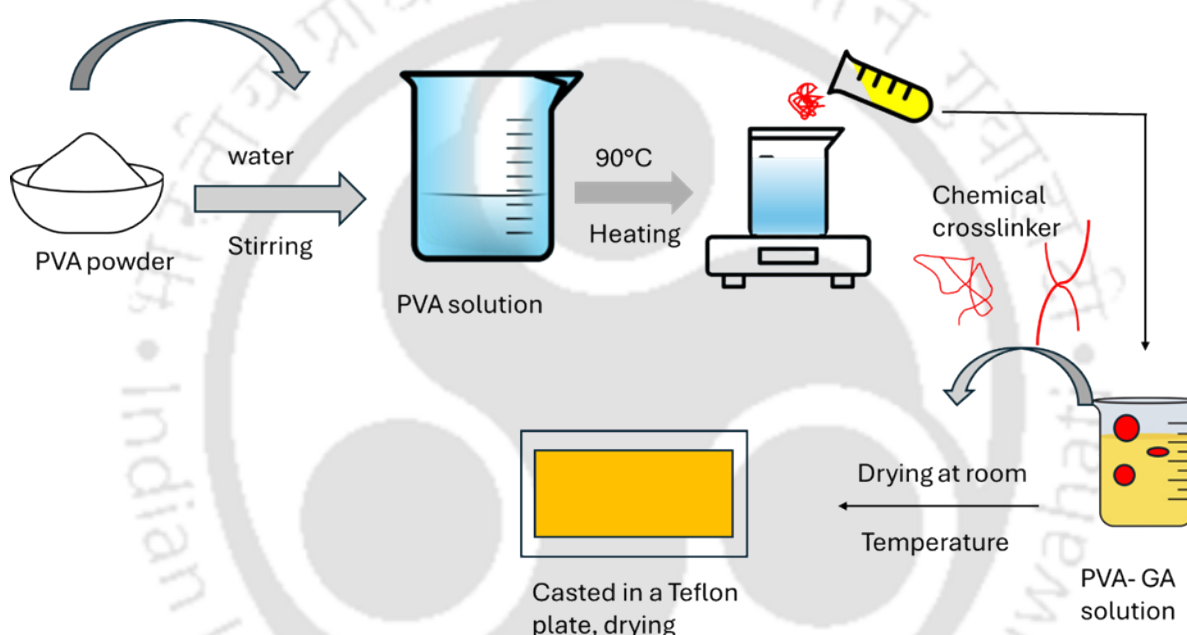


Figure 2.1. Fabrication process of the lab-fabricated membrane

2.1.2. Characterization of the prepared membrane

To estimate water adsorption (WU), membranes were moistened in distilled water. Membrane samples that were 2 cm by 2 cm were immersed in room temperature water for the whole night. The samples were carefully wiped with tissue paper after the surface water was eliminated, and then they were weighed. The swelling percentage was computed using the method described on [232]. The source of the bacterial growth media was wastewater collected from the IIT Guwahati Wastewater Treatment Plant in Amingaon, Assam, India. With a NETSCH DSC 3500 Differential Scanning Calorimeter (DSC), the

variations in the crosslinked membrane's polymer physical characteristics were measured. The DSC thermographs, which were taken at temperatures ranging from 29 to 300 °C at a heating rate of 10 °C/min, consumed around 5.1 mg of the samples. Advanced spectroscopic and chromatographic techniques were used to characterize crosslinked polyvinyl alcohol (PVA) membranes. The RBD- upgraded PHI-5000 Versa Probe III system from PerkinElmer and X-ray photoelectron spectroscopy (XPS), which comprised a monochromatic Al K α X-ray source running at a 55 eV pass energy, were used to analyse the surface chemical composition. The crosslinked PVA membranes' molecular structure and functional group interactions were examined using Fourier Transform Infrared (FTIR) spectroscopy in Attenuated Total Reflectance (ATR) mode. Thermo Gravimetric Analyzer (TGA) (Netzsch, Model: STA449F3A00) was used to perform thermogravimetric analysis (TGA) in an argon environment throughout a temperature range of 25 to 500 °C at 10 °C per minute of heating. About 6–7 mg of sample mass was used. Substrate crossover was examined using High-Performance Liquid Chromatography (HPLC) (Shimadzu Prominence HPLC System, Singapore) equipped with a Refractive Index (RI) detector to aid in chromatographic separation. 0.005 M H₂SO₄ was present in the mobile phase, which was maintained at a constant flow rate of 0.6 L/min. The system worked with a column temperature of 38 °C, an injection volume of 20 μ L, and UV detection set at 210 nm [41]. The anolyte and catholyte were transferred using a syringe to the tiny MFC's input through the specially designed heart-shaped micromixer flow channel. When the voltage started, a fresh anolyte solution was pumped with a new syringe into the anode chamber. A data logger that was attached to the MFC was used to track the voltage. To attain a steady voltage, new anolyte and catholyte solutions were injected and left overnight. The potassium dichromate oxidation method was used to measure the COD levels in the tiny DCMFC's influent and effluent. After the first two hours of digestion at 150 °C in a thermoreactor, the digested material was examined using LR COD Vials, Hach, and the COD value was measured using a DR900 portable colorimeter. The reagent vials used for digestion are HI93754C-25. Following each fed-batch cycle of 48 hours of operation, the anolyte sample was taken. Throughout the entire experiment, three separate measurements were made at a temperature of 30 °C. An Oxford Cypher (AFM) in contact mode

was used for the analysis of the AFM. The photos were taken with a $10\ \mu\text{m} \times 10\ \mu\text{m}$ scan field. The Gwyddion program was used to create the three-dimensional pictures. A Drop shape analyser (Model: DSA25, make: Kruss) was used to assess the contact angle (CA) for both pure PVA and lab-fabricated crosslinked PVA-GA membranes using the sessile drop method.

2.2. Fabrication and assembly of miniaturized MFC device

The miniature microbial fuel cell (MFC) was constructed by stacking Poly (methyl methacrylate) (PMMA) chambers for the anode and cathode, along with a charge separator, in a sandwich configuration (**Figure 2.2**). The anolyte and catholyte were transferred using a syringe to the tiny MFC's input through the specially designed heart-shaped micromixer flow channel as shown in **Figure 2.3**. The incorporation of the heart-shaped flow channel in the microbial fuel cell is inspired by biomimetic microfluidic geometries that are known to enhance mixing under laminar flow conditions. The heart-shaped geometry increases the residence time of substrate and facilitates more uniform distribution of nutrients and electroactive species across the electrode surface, thereby improving biofilm activity and electron transfer efficiency. Similar effects have been reported, like wang et al. 16 [7] reported that structured microchannels enhance mixing and increase residence time, leading to improved performance. Similarly, Strock et al. Demonstrated geometric irregularities induce mixing efficiency without any requirement for increased flow[8] To ensure the chambers were free from contamination, a decontamination procedure outlined in reference [233] was followed before assembling them. Microtubing holes were aligned to establish the influent and effluent pathways. The analytic solution, containing the growth medium, was passed through the anode chamber, while the cathode chamber received the Fe (III) solution as the catholyte. The fabricated membrane, carbon graphite felt electrode, and PMMA components were manually stacked. To verify the integrity of the setup and ensure there was no cross-leakage of flow, sterile water was streamed through the system. This step was performed to confirm that there were no unintended

connections or leaks between the chambers and that the pathways for the analytic and catholyte solutions were properly sealed. The absence of any leakage was crucial to maintaining the separation between the cathode and anode compartments and ensuring an accurate evaluation of the MFC's performance.

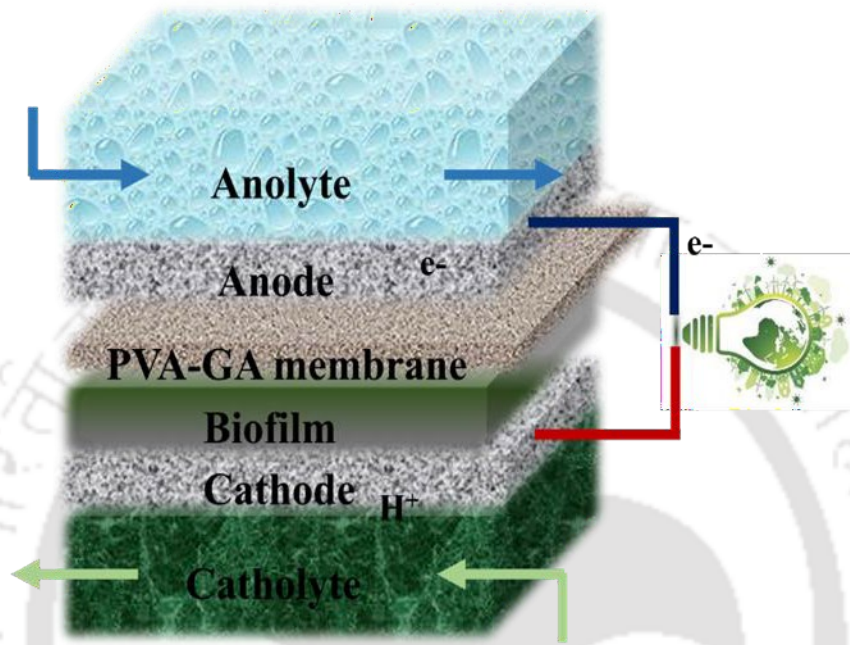


Figure 2.2. Operating principles of a miniature MFC with bacterial growth at the anode and electron transfer through an external circuit

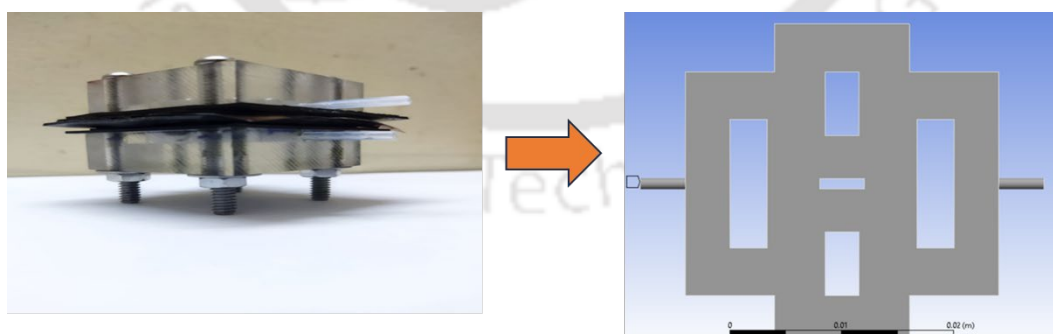


Figure 2.3. Biomimetic heart-shaped microfluidic flow channel in MFC

2.2.3 Smart data Acquisition system set up and performance analysis

The monitoring framework operated using a multi-channel Tracking voltage generation

throughout a small DCMFC simultaneously using an Arduino UNO microcontroller. An ADC converter was integrated with an external 16-bit ADC (ADS1115) module, which was then interfaced with the Arduino UNO board to ensure high-accuracy analogue voltage measurements. In order to timestamp recorded data, the data logger included an RTC (real-time clock) module, which was stored on a micro-SD card in a text file format. The stored data was later retrieved and converted into an Excel file for further analysis. The developed data logger simultaneously monitored voltage generation from ten MFCs for 120 hours, recording potential/voltage readings at 1-minute intervals. Additionally, the voltage readings were measured manually using a Mastech MAS830L multimeter at predetermined times. Data collected from both the fabricated data logger and the commercial multimeter were analysed following the protocol outlined in [234]. With the use of specialist software, the PCB circuit board was computationally developed, making it easier to optimize the arrangement and connections of electrical components on a digital platform. A schematic design was made using KiCad software, connecting cables to parts including the microcontroller, ADC converter, and OLED display as shown in **Figure 2.4**. Then, using the routing tools in the program, traces were created between the microelectronic device pins. The routing topology, tracing width, and spacing were carefully considered to guarantee signal integrity, thermal control, and simplicity of assembly. The design was then validated, and performance under various operating circumstances was predicted using LTspice®. After everything was finished, a Gerber file was created to make manufacturing easier.

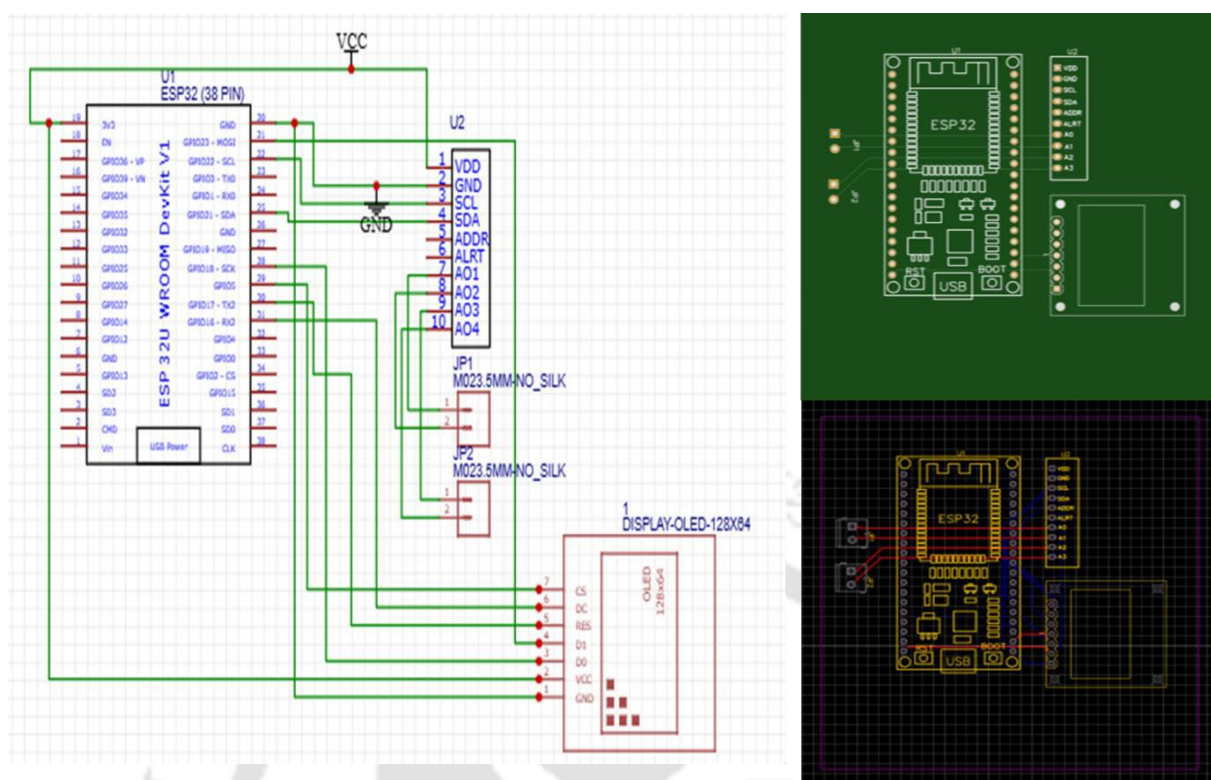


Figure 2.4. Schematic diagram of smart data logging system

2.2.3. Electrochemical behaviour of miniaturised MFC

The electrical output of the miniature MFC was continuously recorded at one-minute intervals. When a voltage drop was observed, a new solution was refilled [235]. The acclimation step for the mini MFC setup was performed to obtain stable conditions for the system [236]. Power (P), voltage (V), and electric current (I) were denoted by their conventional symbols. The schematic and experimental setup are shown in **Figure 2.5**. To get the current density, the measured electricity was divided by the predicted region of the anode. The CH instruments Electrochemical Analyzer (CHI6044E) was used to record the results of the electrochemical impedance spectroscopy (EIS) study. ZsimpWin was used for the analysis of the EIS data. Using the anode surface area (mW/cm^2). Cyclic voltammetry was used to better understand the mixed culture's bioelectrochemical activity using Ag/AgCl as the reference electrode [237]. Coulombic efficiency is defined as the ratio of electrons recovered as electrical current to the theoretical electrons obtainable from complete substrate oxidation. In this work, Acetate

serves as the principal substrate in the anode chamber. Columbic efficiency was ascertained by integrating the measured current over time and comparing it with the theoretical charge derived from substrate consumption according to Faraday's law [238].

2.3. Preparation of the Composite Film

First, a wet laboratory conducting the preliminary trials standardized a film containing chitosan, WCPE. First, 50 mL of distilled water containing 3 wt% glacial acetic acid was used to dissolve 1 wt% chitosan (1 g in 100 g total solution), which was then continuously stirred for two hours at 700 rpm and 60 °C. Simultaneously, 1 wt% cellulose acetate was dispersed in 50 mL of distilled water and stirred under the same conditions. After 2 hours, both solutions were mixed and allowed a residence time of 2 hours at 60 °C for thorough blending. The heating was then stopped, and after the solution reached ambient temperature, 0.3 wt% glutaraldehyde (relative to the total solution weight) was added as a crosslinking agent. A homogenizer (T25 digital ULTRA TURRAX, IKA, USA) and Ultrasonication were used to homogenize the final solution at 6700 rpm until a clear and consistent mix was achieved. To help remove trapped air bubbles, the generated solutions were allowed to equilibrate for one to two hours after homogenization. The resulting solution was ultimately placed on a Teflon plate and subsequently dried for 72 hours at 60 °C using solvent casting to form the film. After being carefully removed, the film was stored at room temperature in a desiccator for future analysis and usage. The structural, optical, mechanical, and thermal characteristics of the dried films were then assessed.

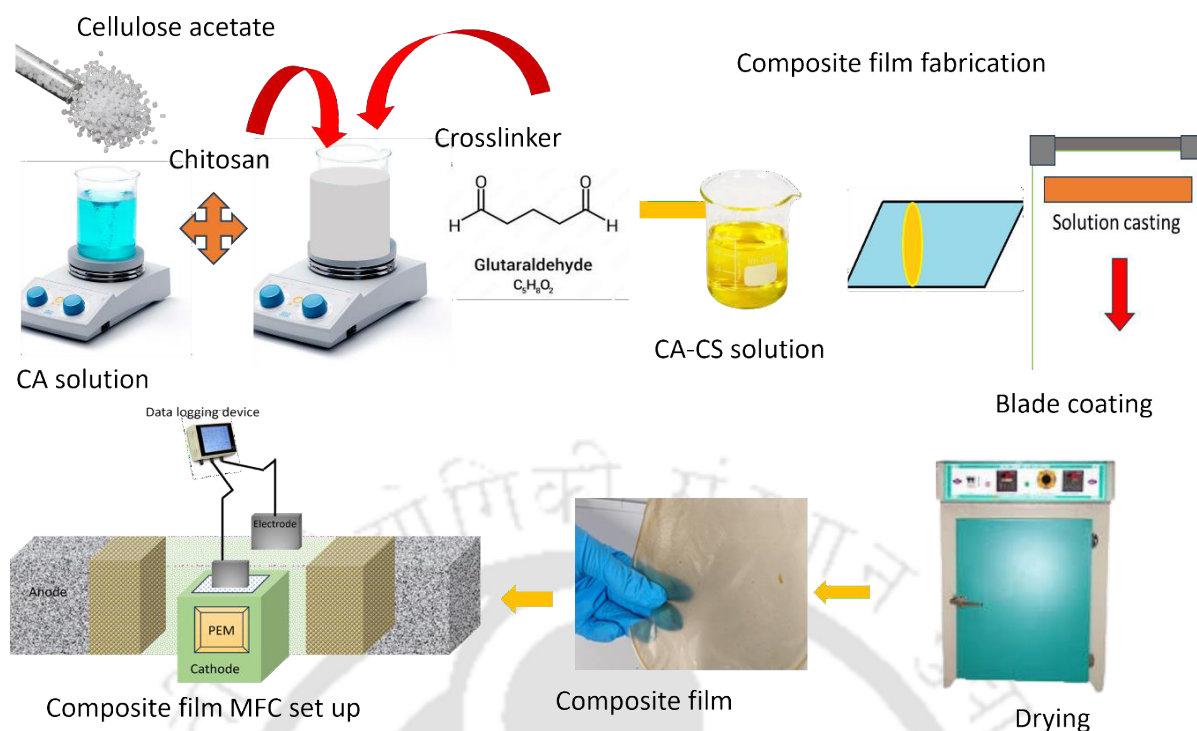


Figure 2.4. Schematic representation of composite film fabrication and application MFC as proton exchanger

2.3.1. Characterization of the membrane

For a full day, the fabricated film was submerged in deionised water to measure water absorption. The mechanical stability and hydration properties of the membrane were assessed by comparing the weights before and after submersion to determine the water absorption capacity. The film's thickness was measured in micrometres using a digital micrometre (Thickness Gauge 7301, Mitutoyo, Japan). Ten different places on each film were used to measure thickness in order to ensure accuracy and consistency. Fourier-transform infrared spectroscopy (FTIR) was used to examine the functional groups on the surface of the proton exchange membrane (PEM) (Spectrum One, PerkinElmer, USA). Surface characteristics were examined using a Field Emission Scanning Electron Microscope (FE-SEM) (JSM-6701F, JEOL, Japan). Energy-dispersive X-ray spectroscopy (EDX) was also used to determine the PEM's elemental composition, providing detailed information about its structural and chemical properties. X-ray diffraction (XRD) spectroscopy was employed to investigate the crystalline

structure of crosslinked bio-composite membranes using a Rigaku TTRAX, Seifert XRD 3003 T/T model. Cu-K α radiation ($\lambda = 0.1541$ nm) served as the X-ray source, and measurements were taken with a 0.02° step size throughout a 2θ range of 3° to 80° . The OCA15+ goniometer system (Dataphysics, Germany) measured contact angles. For analysis, thin, 1×1 cm rectangular specimens were made. Contact angles were measured after milli-Q water droplets ($2 \mu\text{L}$ each) were applied to the sample surfaces at room temperature. To ensure the reliability of the results, the standard deviation was calculated, and at least three reproducible measurements were made from duplicate samples for precision. An AFM investigation was conducted to compare the surfaces of composite membranes in terms of the roughness parameter. Using the roughness parameters derived from the AFM pictures as the absolute roughness value is not appropriate. Differential scanning calorimetry (DSC) was done in Q200 DSC(TA Instruments, United States) at a heating rate of $20\text{--}250^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. The second heating of $20\text{--}250^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ was used to calculate the glass transition temperatures (T_g). Using a PerkinElmer TGA 4000 system, thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the crosslinked membrane. The examination was performed in a nitrogen (N_2) environment with a temperature range of 30 to 700°C and a constant heating rate of $10^\circ\text{C}/\text{min}$. This process allowed for the evaluation of the membrane's degradation profile and thermal resistance. We used 5KN universal testing equipment (Z005TNProline, manufactured by Zwick Roell in India) to check the samples' mechanical qualities. To perform the mechanical analysis, each sample was divided into rectangular pieces, and the assessment was carried out at a speed of $5 \text{ mm}/\text{min}$. The cross- section of the tested sample is automatically calculated using the entrance characteristics, such as width and thickness. The humidity was about 34% and the room temperature was set at 25°C . One hundred millimetres per minute of strain was applied during the tensile test. The presented results are the mean of at least five independent measurements taken from the same sample to guarantee precision and dependability. The

biofilm-forming bacterial strains *Staphylococcus aureus* and *Escherichia coli* in Luria-Bertani (LB) broth were used in a conventional crystal violet experiment to evaluate the modified membranes' antibiofilm activity. Ten millilitres of sterile LB broth were injected with a single colony of the chosen bacterial strain, which was then shaken at 150 rpm for the duration of the incubation period at 37 °C. After 72 hours of incubation, sterile membrane samples (1 cm × 1 cm) were individually added to the bacterial medium and examined [239]. After incubation, sterile phosphate-buffered saline (PBS, pH 7.4) was used to gently wash the membranes three times to remove any loosely attached bacterial cells. To examine the morphology of the microorganisms on the membrane surface, a FESEM (JSM-6500F) was utilised. The samples were fixed in 2.5 wt% glutaraldehyde, washed three times in buffer, and then successively dehydrated in 10%, 50%, 70%, 80%, 90%, and 100% ethanol/water solutions for 30 minutes each. The samples were allowed to dry undisturbed. They were sputtered with platinum in a vacuum before examination using FESEM.

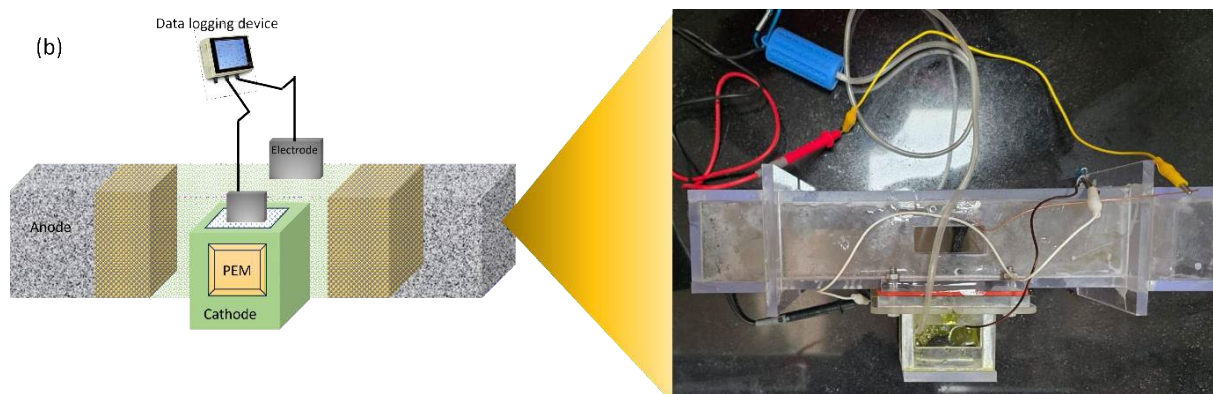


Figure 2.5 (a) The complex matrix of hospital wastewater, (b) Physical model of composite film-based MFC

2.4. Double chambered bio-electrochemical fuel cell (DBEC) fabrication and operation

A dual-chamber microbial fuel cell, as shown in Figure 2.4. was built and constructed to evaluate the efficacy of the developed membrane for a 50 mM $K_3Fe(CN)_6$ (Sigma Aldrich) catholyte. All electrodes used in this investigation included 0.12 g samples of GF. The source of the mixed bacterial culture was hospital-derived wastewater collected from the local medical dispensary located in Amingaon, Guwahati, India. A 50mM phosphate buffer nutrient solution and wastewater containing a mixed bacterial culture were combined in a 1:1 ratio with the inoculum in the anode chamber of both MFC modules. The PBS formulation contains 2.45 gram per litre $NaH_2PO_4 \cdot H_2O$, 4.58 g/L Na_2HPO_4 , 0.13 g/L KCl, and 0.31 g/L NH_4Cl . The preliminary concentrations of Hospital wastewater (HWW) contained ammonium nitrate 6500ppm, Salinity 5.5 ppt, pH 5.33, TDS 1.35 ppt, COD 1161mg/L, chromium <1ppm, DO 6.2mg/L, at 25°C. The anticipated electrode surface area was comparable to the anode surface area, measuring 5 cm², while the internal volume of both the cathodic and anodic chambers of the MFC was 1 L each. All tests were conducted at a temperature of 30°C, and measurements were taken in triplicate.

2.5. Electrochemical measurement and Biofilm Analysis

All necessary connections were established using stainless-steel wires, and an external resistance of $1\text{K}\Omega$ was affixed across the two electrodes. The anodic sides were sealed airtight to maintain the anaerobic environment in the anodic chamber of the MFC. The MFC functioned in batch mode, with wastewater refilled upon reaching baseline voltage. The MFC was run for 30 days during this time, and its performance was assessed. A Sanwa CD7711 digital multimeter was used to continuously measure the voltage across the load at one-minute intervals. The observed voltage was then transformed into current using Ohm's law: $\text{Voltage} = \text{Current} \times \text{Resistance}$. EIS analysis was used to determine MFCs' internal resistance, conducted using a CHIE Photo Electrochemical Workstation (India). During the EIS experiment, a sine wave with an amplitude of 10 mV was delivered in sweep mode, ranging from a frequency of 100 kHz to 0.1 Hz. The potassium dichromate oxidation method was used to calculate the effluent's chemical oxygen demand. Before analysis, the 2 mL wastewater sample in the HR COD vials, K-K-K-7360S from Suntex, was digested for two hours at $150\text{ }^{\circ}\text{C}$ in the TR-1100 COD Thermoreactor made by Suntex Instruments Co., Ltd. Every fed-batch cycle, which typically lasted 24 hours, had anolyte samples taken at the start and end. The photometric measurement was conducted after the digestion of the COD vials. Both modules were examined using field emission scanning electron microscopy (FESEM) to evaluate microbial colonization on the anode surface. After preserving microbial structures by first fixing electrodes with biofilm in a 2.5 wt% glutaraldehyde solution, the electrodes were rinsed three times with phosphate-buffered solution to remove any remaining fixative. For additional dehydration, a sequence of graded ethanol (30%, 50%, 70%, 80%, 90%, and 100%) was employed. Each phase lasted 30 minutes to guarantee a slow loss of water while preserving cellular integrity. Additionally, clean (microbe-free) anodes were photographed for comparison in order to confirm the presence of microorganisms and differentiate surface artefacts from biofilm growth.

2.6. Fabrication of modified membrane

Graphene oxide (GO) was synthesised by the modified hummers process, which provides a more efficient and ecologically friendly alternative to the traditional Hummers approach [240], [241]. Cellulose membranes with a pore size of 0.45 μm and a diameter of 47mm were used. D- Glucose (Sigma-Aldrich), Ampicillin (chemical formula: $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}_4\text{S}$, molecular mass: 349.4 g/mole) was purchased from Sigma-Aldrich Co., USA. All other chemicals required for experimental work were procured in analytical grade. To prepare 0.2, 0.4, 0.6, 0.8, and 1.6 wt% graphene oxide (GO) in polyvinyl alcohol (PVA) solution, a predetermined amount of GO was dispersed in deionised (DI) water using ultrasonication to ensure uniform exfoliation and stability of the nanosheets. Separately, PVA was dissolved in DI water by continuous stirring and heating (80–90 $^{\circ}\text{C}$) until a transparent solution was obtained. Polyvinyl alcohol (PVA) acts as an effective binder for graphene oxide (GO) in cellulose-based membranes. PVA is hydrophilic, has adjustable viscosity, and is an effective film-former, facilitating the regulation of withdrawal speed-thickness correlations during dip coating. PVA has a high concentration of hydroxyl ($-\text{OH}$) groups throughout its polymer backbone, enabling substantial hydrogen bonding with the oxygen-containing functional groups present on GO sheets and the hydroxyl groups on cellulose. This bidirectional interaction guarantees robust interfacial adhesion between GO and the cellulose matrix, inhibiting phase separation and improving dispersion uniformity [242]. The dispersed GO suspension was added dropwise to the PVA solution while continuously stirring to prevent agglomeration, followed by ultrasonication for complete homogenization. Each membrane was thereafter submerged in the GO dispersion for a predetermined time to provide adequate adsorption of GO nanosheets onto the polymeric surface and inside the superficial pore architecture. The coated membranes were then dried at ambient temperature or in a controlled oven to eliminate moisture and improve the adhesion between the GO layer and the CE matrix. Finally, four membranes were formed with different

GO loading named CEGO-1 (0.2 wt%), CEGO-2 (0.4 wt%), CEGO-3 (0.6 wt%), and CEGO-4 (0.8 wt%) as shown in **Figure 2.6**.

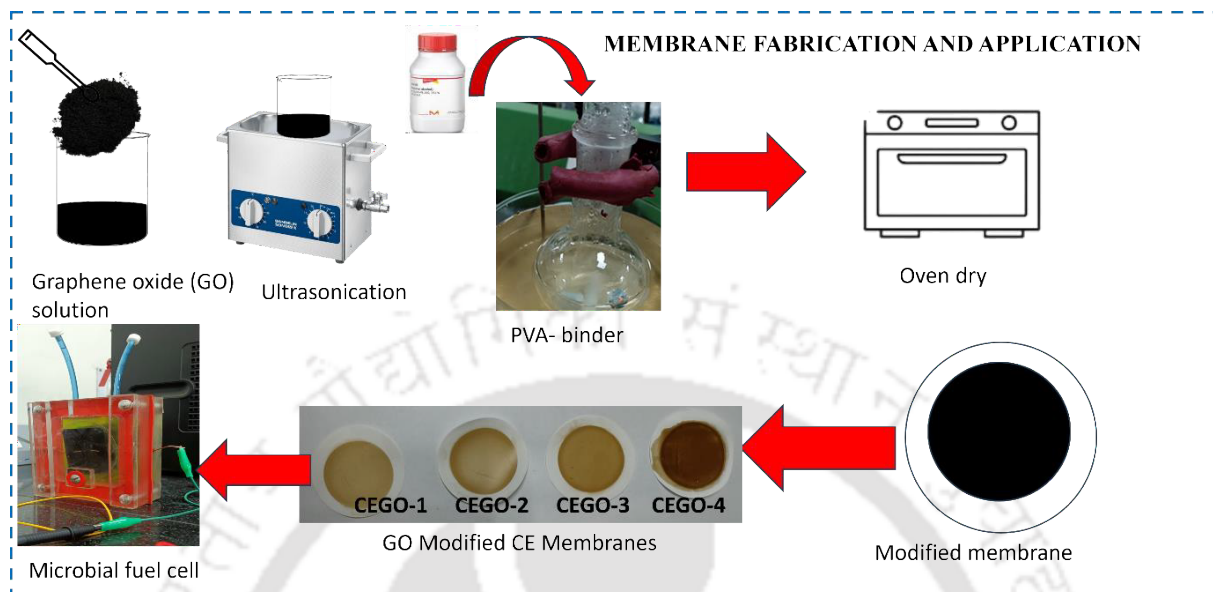


Figure 2.6. Fabrication process of the synthesized membrane

2.6.1. Modified membrane Characterization

Water uptake (WU) was quantified by assessing the weight differential of the membrane samples pre- and post-hydration. Membrane samples (2 cm x 2 cm) were submerged in distilled water at ambient temperature for one night. Upon removal, surface moisture was delicately absorbed using tissue paper, and the hydrated samples were promptly weighed. Modified membranes were characterised by Fourier transform infrared (FTIR) spectroscopy (using a PerkinElmer Frontier FTIR Spectrophotometer system) for structural analysis, which was carried out in ATR mode. The crystalline nature of the modified membranes was evaluated through X-ray diffraction (XRD) spectroscopy (Rigaku, Model: Micromax-007HF) in the range of $2\theta = 3\text{--}60^\circ$, with a 0.02° step size, using Cu-K α radiation ($\lambda = 0.1541\text{ nm}$) as the X-ray source. Raman spectroscopy was used to examine the molecular interactions between graphene oxide (GO) and the cellulose ether (CE) polymer matrix. Measurements were conducted with a Horiba Jobin Yvon LabRam HR system with a 632 nm excitation laser. Spectra were

obtained within the range of 200–4000 cm^{-1} , using a 5-second acquisition period and a single accumulation per sample to guarantee repeatability and reduce temperature effects. Contact angles were measured after milli-Q water droplets (2 μL each) were applied to the sample surfaces at room temperature. X-ray photoelectron spectroscopy (XPS) was used to examine the chemical composition of the membrane. Thermo Gravimetric Analyzer (TGA) (Netzsch, Model: STA449F3A00) was used to perform thermogravimetric analysis (TGA) in an argon environment throughout a temperature range of 25 to 500 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}$ per minute of heating. About 6.5 mg of sample mass was used. An Oxford Cypher (AFM) in contact mode was used for the analysis of the AFM. The photos were taken with a 10 $\mu\text{m} \times 10 \mu\text{m}$ scan field. The Gwyddion program was used to create the three-dimensional pictures. The mechanical properties of the membranes were evaluated using a 5 kN universal testing apparatus (Z005TN ProLine, Zwick Roell, India). Each membrane was cut into rectangular strips, and tensile tests were conducted at a crosshead speed of 5 mm/min. The gadget independently calculated the cross-sectional area using the given parameters (width and thickness). Experiments were performed under controlled ambient conditions of about 34% relative humidity and 25 $^{\circ}\text{C}$. A strain rate of 100 mm/min was consistently used throughout the tensile investigation. The provided findings are the average of at least five independent measurements obtained from each sample to ensure reliability and statistical accuracy. The antimicrobial properties of the treated membranes were evaluated using *Escherichia Coli* as the model organism. LB media (1 L) was prepared and subsequently sterilised via autoclaving for a duration of 30 minutes. After sterilisation, two flat-bottom flasks containing the medium were inoculated with the bacterial species. The cultures were then cultivated in an incubator shaker at 37 $^{\circ}\text{C}$ with continuous agitation at 180 rpm. Membrane specimens were placed in bacterial culture and incubated for 72 hours to promote microbial colonisation on their surface [243]. For further morphological investigation, the samples were prepared for Field Emission Scanning Electron Microscopy (FESEM, JSM-6500F). The preparation included a first fixation phase with a 2.5 wt%

glutaraldehyde solution. After fixation, the specimens underwent three washes with a buffer solution.

2.6.2. Assembling of the dual-chambered MFC with modified membrane

Double-chamber microbial fuel cells (MFCs) were constructed using a poly(methyl methacrylate) (PMMA) reactor with a capacity of 140 mL. Graphite felt electrodes (SynLectro™, Sigma Aldrich) with a surface area of 5 cm² were used for both the anode and cathode. The electrodes were placed inside the circular chambers, maintaining a 1 cm inter-electrode distance. Titanium wires functioned as electrical connections, and all junctions were sealed with epoxy resin to avert leaking. Unless specified differently, a 1 k Ω external resistance was used throughout the studies. The cathode compartment was filled with 50 mM potassium ferricyanide dissolved in 50 mM phosphate-buffered saline (PBS; 137 mM NaCl, 2.7 mM KCl, 10 mM Na₂HPO₄·2H₂O, 2 mM KH₂PO₄, pH 7.4). The influent pH and conductivity were constantly regulated at 8.2 ± 0.5 and 8.1 ± 1 mS cm⁻¹, respectively. The mixed microbial inoculum was sourced from hospital wastewater collected from a neighboring healthcare facility in Guwahati, Assam, India. This discharge represented a typical source of diverse microbial communities seen in medical wastewater streams. Three membranes were employed for the experimental work: MFC with Nafion, pristine CE, and GO modified CE, named as MFC- A (N), MFC- B(CE), MFC- C (CEGO).

2.6.3. Electrochemical measurement and microbial analysis

The voltage (V) across the external resistance (R) of the MFC was persistently observed using a data gathering device (Sanwa Pc773, Japan). A multichannel electrochemical analyser was used to monitor voltage and current, with data collected at one-minute intervals. The internal resistance of the MFCs was assessed by electrochemical impedance spectroscopy (EIS), conducted with a multichannel electrochemical workstation, and the resultant spectra were

examined using ZView software. Electrochemical impedance spectroscopy (EIS) was conducted using a sine wave with an amplitude of 10 mV in sweep mode, covering frequencies from 100 kHz to 0.1 Hz. The chemical oxygen demand (COD) of the effluent was measured using the potassium dichromate oxidation technique. For this, 2 mL of sample was transferred into COD digestion vials (HR+, pk/150; HACH) and digested at 150 °C for 2 h in a COD reactor (HI839800; Hanna Instruments Pvt. Ltd., India). Analyte samples were collected at the beginning and end of each fed-batch cycle (typically 24 h). The digested COD vials were subsequently analysed using a COD photometer (A-7325; CHE Metrics, India). To ensure microbial adhesion on the anode surface, the anodes of both modules were examined using FESEM (Zeiss Gemini). The sample preparation was performed as described in [244]. To ensure the presence of microbes, the surface morphology of the control electrodes (without microbes) was examined. Transmission electron microscopy (TEM) (JEOL, JEM 2100) was used to examine the microscale morphology of electroactive microbial populations in the activated sludge effluent of the two-chambered MFC system. The investigation sought to clarify the structural organization and electron transport processes facilitated by bacterial extracellular polymeric substances (EPS) linked to the cell walls.

Chapter-3

Per and poly-fluoroalkyl-free PVA membrane separator for sustainable energy recovery from municipal wastewater using Biomimetic miniature microbial fuel cell

Motivation

The widespread use of PFAS-based membranes in microbial fuel cells (MFCs) raises significant environmental, health, and economic concerns, stemming from their persistence, inherent toxicity, and increased production costs. Simultaneously, municipal wastewater represents a largely underutilized resource for sustainable energy recovery via bioelectrochemical systems. Consequently, there is a pressing requirement to formulate environmentally sound, PFAS-free membrane separators that adhere to circular economy principles while ensuring superior electrochemical performance. Poly (vinyl alcohol) (PVA), due to its biodegradability, non-toxic nature, affordability, and adjustable hydrophilicity, presents a potentially advantageous alternative membrane material for MFC applications.

The work in this chapter is published as

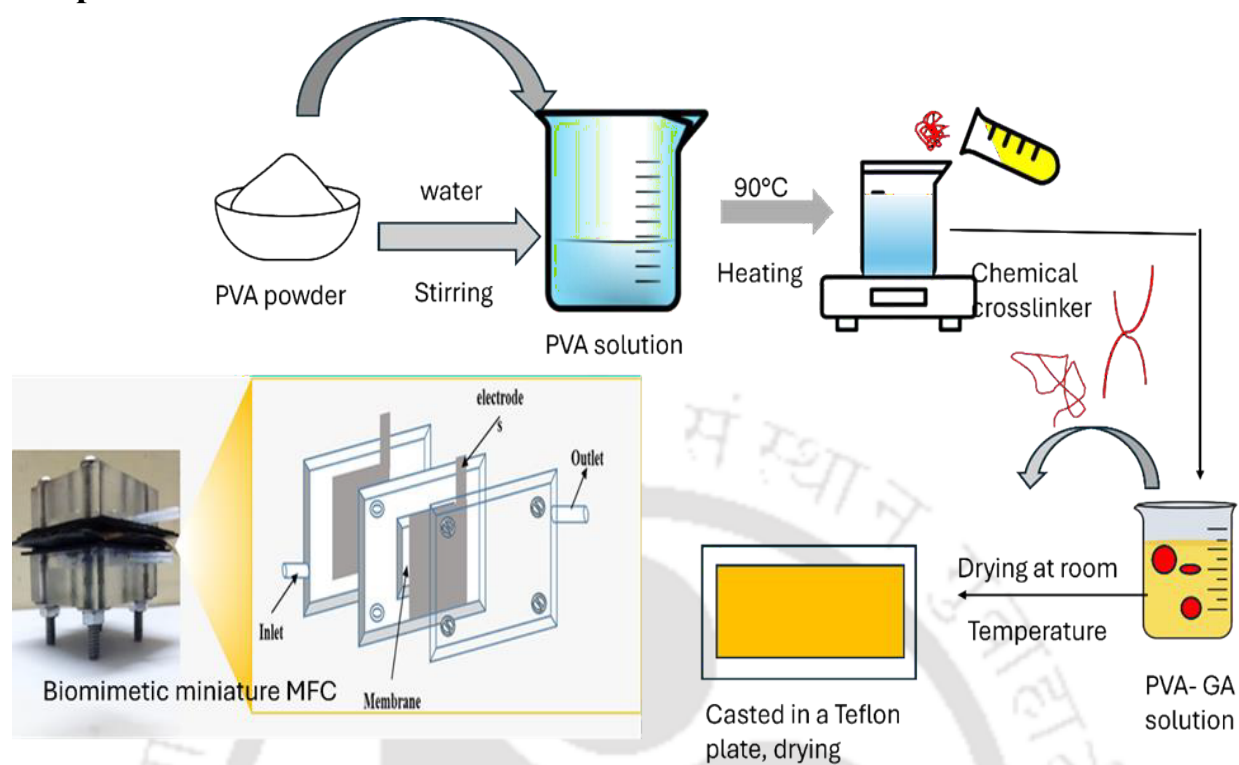
Aparajita Roy, Bhanupriya Das, Sonu Kumar, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, Per and Poly-Fluoroalkyl-Free PVA Membrane Separator for Sustainable Energy Recovery From Municipal Wastewater Using Biomimetic Miniature Microbial Fuel Cell Journal of Applied Polymer Science 2025 Volume 142 Issue - 46 0021-8995

<https://doi.org/10.1002/app.57809> SP - e57809 2025

Abstract

This chapter focuses on the design and integration of a PFAS-free PVA membrane separator within a biomimetic miniature microbial fuel cell. Microbial fuel cells (MFCs) have emerged as a viable alternative in the search for sustainable bioenergy and efficient wastewater treatment. This work introduces the creation of a biomimetic, miniaturized microbial fuel cell (MFC) that utilizes nature-inspired flow channel design and eco-friendly materials to enhance electrochemical performance and reduce overall costs. A micron-scale, heart-shaped flow channel was constructed to provide continuous micromixing of the effluent at both the anode and cathode, enhancing mass transfer, substrate utilization, and bacterial-electrode interactions. A PFAS-free, laboratory-synthesized membrane was used as a charge separator, replacing the conventional Nafion 117 membrane, to eliminate costly and ecologically detrimental components. A custom-designed Arduino-UNO-based smart data recording system was included for real-time voltage monitoring, providing a cost-effective substitute for commercial multimeters. The MFC attained a peak, coulombic efficiency of 85.5% and exhibited a concurrent chemical oxygen demand (COD) elimination efficiency of 68 ± 0.10 % when processing municipal wastewater. A thorough techno-economic study indicated that the overall cost of the system was 46.10 USD /ft², making it around eight times more cost-effective than conventional Nafion-based MFCs. The decrease in costs, together with enhanced electrochemical and treatment efficacy, highlights the system's scalability and practical feasibility for decentralised wastewater treatment and energy production.

Graphical Abstract



3.1. Introduction

Water shortages are an escalating worldwide concern impacting billions, exacerbated by climate change, population growth, pollution, and unsustainable water management practices. Comprehending water shortage is essential for developing policy at the global, regional, national, and local levels. “The Eighth Phase of the International Hydrological Programme (IHP-VIII), which focuses on 'Water Security: Responses to Local, Regional, and Global Challenges (2014–2021),' has six topics, including 'addressing water scarcity and quality' [245]. The water supply problem was named the most significant concern of our time in the World Economic Forum's 2015 Global Risks Report [246]. One of the goals of the newly established Sustainable Development Goals by the United Nations is to "significantly reduce the number of people suffering from water scarcity" [2015] [247]. Pollution from industrial waste, agricultural runoff, and inadequate sanitation further reduces usable freshwater supplies. To combat this crisis, sustainable solutions like wastewater treatment are essential. Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic organic compounds characterized by the partial or complete replacement of hydrogen atoms with fluorine atoms [248]. PFAS have been identified as potentially harmful to both humans and wildlife (OECD, 2013). In the early 2000s, initial studies reported the presence of PFAS in human blood serum and various wildlife species, sparking significant public concern and awareness [249]. The potential health risks linked to PFAS exposure have been associated with several diseases, including ulcerative colitis, thyroid dysfunction, and various forms of cancer [250]. Most membrane preparation procedures use hazardous and ecologically damaging solvents [251]. Growing environmental concerns have emphasized the need for safer membrane fabrication methods that utilize non-toxic, green solvents [252]. The United Nations Environmental Protection Agency (UNEP) established the principles of green chemistry in the 1990s, and these principles serve as the foundation for efforts to create more ecologically friendly membrane production techniques.

These principles emphasize the design of sustainable processes and materials that minimize or eliminate chemical-related contamination. Microbial fuel cells come in a variety of configurations, including single-chambered, double-chambered, and stacked configurations with anode and cathode compartments. Over the years, it has become a robust technology across the globe for researchers working in different areas of it to enhance the performance [253]. Researchers have been working on different architectural aspects of MFC, like electrodes, chemical substrates as feed, microbial inoculum, and low-cost proton exchange membranes as an alternative to high-cost Nafion available commercially [254]. There has been a lot of study into microbial fuel cell (MFC) technology, with an emphasis on developments at the macroscopic level and large-scale uses [255]. Numerous studies have showcased the ability to generate an electric current through MFCs by utilizing carbon as an organic source [256]. However, the electron transfer rate between the electrodes is further reduced because the ionic transport mechanism via the electrolytic route is not quick enough [257]. Also, power loss and ohmic loss are observed at the macroscopic level due to slower ion transport and higher internal resistance [258]. Despite the growing interest in microbial fuel cells (MFCs), limited research has been conducted on miniature micron-scale MFCs for sustainable energy generation, particularly those employing specialized PFAS-free PVA membranes as charge separators. Most reported studies, to the best of our knowledge, rely on commercially accessible Nafion membranes [259], which are costly and environmentally concerning [260]. This dependency confines such research to laboratory or R&D settings, hindering real-world application. Moreover, the widespread use of expensive commercial digital multimeters for system monitoring further escalates operational costs, rendering the approach inefficient and impractical, especially for remote or rural deployments [261]. The reliance on these high-cost components poses a significant barrier to scalability, limiting the transition of micron-scale MFC technology from the lab bench to field-scale implementation. Commercial multimeter dataloggers are widely used for real-time voltage logging in MFC studies. In a study on the

biodegradation of oxalate in human urine, a PROVA-803 multimeter datalogger was connected to a computer to record the open-circuit voltage (OCV) every two minutes [262]. Similarly, in a micron-scale MFC experiment to enhance power and current density, ties were used, using an Arduino UNO-based system that includes four single-ended input channels (DAQ/68, National Instruments) [263]. In another experiment with a sustainable, macro-scale MFC of 3L volume, the voltage potential (mV) between the electrodes was monitored daily using a digital multimeter. (UNI-T UT33A, China) [264]. Commercial data recorders offer high automation and precision in microbial fuel cell (MFC) experiments, but they come at a premium cost.

In that context, micron-scale MFC plays a vital role wherein such devices' power output continuously increases due to its special microfabrication technique, which has been adopted for better performance in the wastewater treatment phenomenon [265]. There are many benefits to building small MFC devices, including the ability to use a broad range of wastewater as feedstock, mixed culture bacteria as biocatalysts, and an operational temperature selection [266]. It is also useful for the ease of studying microbial communities in a microenvironment responsible for the maximal potential of MFCs [267]. As previously reported, a considerable quantity of small-scale MFCS units interconnected will generate more electricity than a solitary big one [268][269]. An optimal separator must exhibit hydrophilicity, minimal resistance, and enhanced ion transport capabilities and selectivity [270]. There have been records of using membrane-less MFCs, but it was found that in the absence of a membrane, the system efficiency gets decreased due to the increased rate of uptake of oxygen and external substrates, affecting the catalytic activity of microorganisms present in the anode compartment [271]. Increased substrate diffusion causes rapid biofouling and deactivation of the catalyst if present in the cathode compartment, leading to a significant loss in the overall performance of the MFC. Nafion membrane accounts for approximately 38% of the whole fuel cell expenditure [272], [273]. The cost of Nafion-117 is approximately \$33.00 for a 10×10 cm sheet a member of the per- and polyfluoroalkyl substances (PFASs) group, Nafion raises environmental concerns due

to its persistence and potential ecological impact [274]. Moreover, Nafion requires activation using corrosive chemicals such as hydrogen peroxide and sulfuric acid. In contrast, an inexpensive, non-toxic, hydrophilic, and biodegradable substance, polyvinyl alcohol (PVA), provides a more environmentally friendly and financially feasible substitute for traditional membranes such as Nafion-117. Recently, PVA-blended membranes have been widely utilized in hemodialysis (HD) owing to their protein antifouling and biocompatible properties, making them effective in removing creatinine and higher molecular weight contaminants [275]. In their crosslinked form, they provide an innovative and sustainable approach to addressing this challenge. In contrast to conventional crosslinked polyvinyl alcohol (PVA) membranes, they are a major improvement over PFAS-based Nafion-117 membranes, which are expensive, prone to biofouling, and require chemical activation [276]. They offer superior cost-effectiveness, catalyst-free operation, environmental sustainability, and dependable performance [154] [277][278]. Beyond cost and effectiveness, crosslinked PVA in tiny MFCs is significant because it establishes it as a sustainable substitute for PFAS-based Nafion-117 membranes in energy-efficient wastewater treatment. From a secure position standpoint, employing PVA membranes in municipal wastewater systems helps tackle two critical issues: reducing exposure to harmful pollutants and preventing the environmental discharge of untreated PFAS compounds [279]. Moreover, the energy recovery potential of miniature MFCs equipped with PVA membranes positions them as a sustainable solution for healthcare facilities, particularly as biosensors. By meeting strict discharge regulations and effectively addressing PFAS removal, this technology not only ensures regulatory compliance but also reduces the effect on the environment and creates cleaner water systems.

This work specifically investigates PVA membranes inside a micron-scale biomimetic microbial fuel cell for the treatment of municipal wastewater. The environmentally sustainable membrane presents a viable substitute for expensive membranes, augmenting proton conductivity, ion separation, and the elimination of organic substances, hence boosting

electrochemical efficacy and ecological sustainability.

The intended purpose of this research is to create inexpensive, GA-crosslinked biodegradable PVA membranes and assess their potential for usage as proton exchange membranes in biomimetic tiny microbial fuel cells, which utilize actual municipal wastewater as an anolyte to generate energy applying and assessing a smart data logging system based on an inexpensive microcontroller in a miniaturized MFC and utilizing specific flow channels, investigating the initial removal of lead as one of the heavy metal in a miniaturized MFC based on a separator produced in the lab. The performance of the GA- crosslinked PVA membrane is compared with commercial Nafion-117 based on physicochemical properties, heavy metal removal, internal resistance, COD removal, bioelectrochemical analysis, and cost-effectiveness to assess its practical application in a miniature MFC.

3.2. Results and Discussion

The comparison between Nafion 117 and the crosslinked PVA membrane is superficial and incomplete, even if the latter is rarely used in this specific MFC field. While the cost-effectiveness of the membrane is of significant benefit, its practical usability necessitates a comprehensive performance evaluation rather than just a cost-based comparison.

3.2.1. Water adsorption and swelling

The water adsorption and swelling capabilities of PVA–GA (polyvinyl alcohol–glutaraldehyde) membranes are essential for their efficient operation, especially in applications such as microbial fuel cells. PVA is a very hydrophilic polymer that absorbs water quickly because of its many hydroxyl (-OH) groups, which can create hydrogen bonds with water molecules. When crosslinked with glutaraldehyde, certain hydroxyl groups create acetal linkages, which limit the number of free -OH groups accessible for water interaction and create a three-dimensional network structure. Therefore, the amount of water adsorption reduces as

the crosslinking density increases. The swelling of the membrane is significantly influenced by the degree of crosslinking. Physical expansion results from water ions penetrating the polymer matrix when it is swelled; however, a larger crosslink density restricts the mobility of polymer chains, which in turn restricts the swelling ratio. A well-crosslinked PVA–GA membrane maximises water absorption for efficient ionic conduction while reducing excessive swelling that can jeopardise mechanical integrity. A gravimetric method was used to determine the water uptake, adsorption and swelling behaviour using the technique used in earlier studies [9]. Membrane samples were dried to constant weight, and the initial dry weight (W_1) was noted. The samples were then equilibrated by placing in deionized water at ambient temperature, and allowed to equilibrate (24 h). Excess surface water was then blotted off with the assistance of tissue paper, and the hydrated weight (W_2) was recorded immediately after removal. The water uptake (WU, %) and swelling (%) were determined. Therefore, the swelling was assessed concerning gravimetric (weight-based) expansion as opposed to dimensional (area or thickness) shifts. The water absorption of pure PVA was found to be $270 \pm 0.12\%$ as shown in **Figure 3.1**. On the incorporation of the crosslinker, there was a significant reduction in water absorption to $60 \pm 0.2\%$. Likewise, the ratio of swelling decreased in value before crosslinking, $60 \pm 0.2\%$ and after crosslinking, $25 \pm 0.03\%$, which means that there was an increase in the structural stability of the membrane.

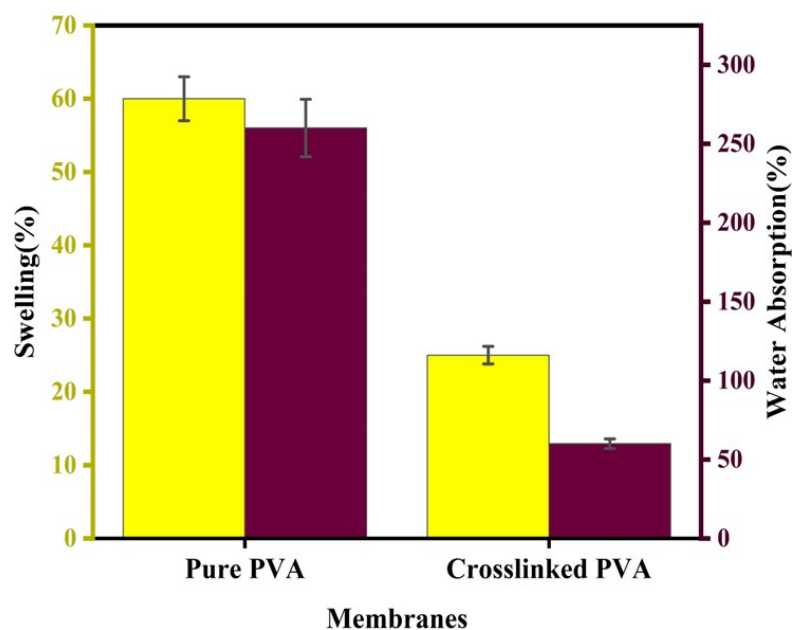


Figure 3.1. Swelling and water absorption of pure and crosslinked PVA separator

3.2.2. FTIR and Thermal Analysis

The infrared spectra of pure PVA and PVA-GA membranes used as separators are displayed in **Figure 3.2(a)**. Pure PVA and blended PVA-GA have spectra that are almost identical to the spectrum at 3258 cm^{-1} . PVA's hydrogen-bonded hydroxyl group's O-H stretching properties. Both C and H are symmetrical and asymmetrical. Stretching symmetrically and asymmetrically from C to H at 2920 cm^{-1} and 2845 cm^{-1} , respectively assigned to C-H stretching modes of PVA backbone on crosslinking, C-H bending at 1427 cm^{-1} , C-H vibration at 1321 cm^{-1} , C-O stretch at 1091 cm^{-1} due to acetal linkage, O-H out of plane deformation at 910 cm^{-1} and C-C stretch at 830 cm^{-1} [280]. However, in the PVA-GA graph, we can see that the C-O-C stretch is being observed at PVA-GA, which confirms the crosslinking process [281]. Furthermore, the C=O peak observed at PVA is due to the branching of PVA, which is brought on by GA producing aldehyde side chains seen at 1747 cm^{-1} [282]. The TGA Curve in **Figure 3.2 (b)** illustrates the results of thermal analysis of the cross-linked membrane and pure PVA. Both samples show two-step mass loss, one up to 160°C and the other up to 360°C . In particular, pure PVA demonstrates that mass loss begins at 39°C and that the residual mass

stabilizes at 120°C. On the other hand, mass loss in the PVA-GA separator begins at about 85°C, and the residual mass stabilises at about 164°C.

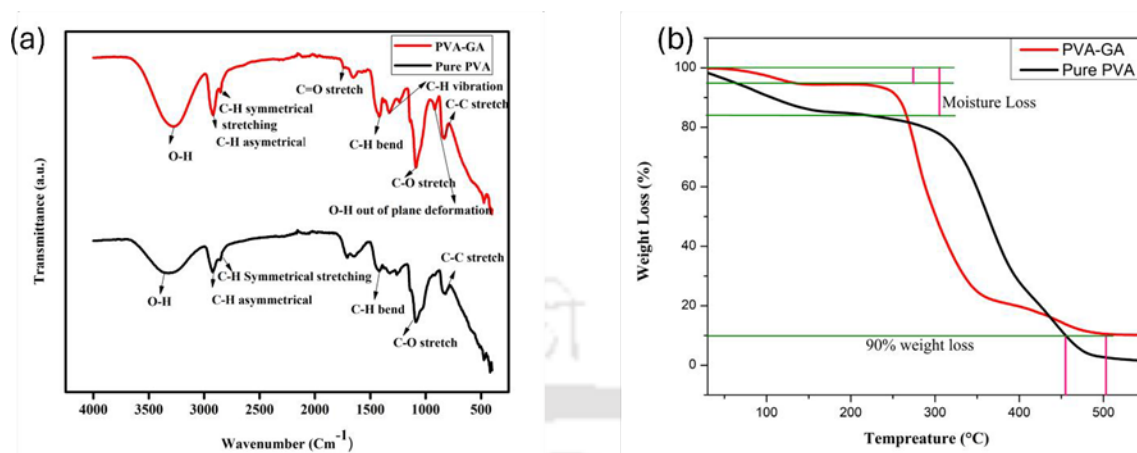


Figure 3.2. (a) FTIR and b) TGA of lab-fabricated membrane

3.2.3. DSC and XPS analysis

The PVA-GA lab-fabricated membrane's thermal stability is further demonstrated by the DSC curve in **Figure 3.3 (a)**, which displays T_m at 215°C and T_g at 80°C in a humid environment. This aligns with the data that has been recorded in scholarly works of literature [283]. The rise in T_g values of these cross-linked PVA separators is remarkably similar to that previously seen in the literature [284]. The melting of crystalline areas in the PVA matrix is represented by the strong endothermic peak at 215 °C. The semi-crystalline PVA structure's dual-phase nature is reflected in these temperature changes, especially following chemical crosslinking like that with glutaraldehyde (GA). The glass-rubber transition of the PVA-GA membrane's amorphous portions is represented by the observed T_g value. Because the OH group of PVA and the aldehyde group of GA limit the mobility of the polymer chain. The graph shows that the GA contents have a significant impact on the melting temperature (T_m). The crosslinked membrane's XPS spectra, which are displayed in X-ray photoelectron spectroscopy (XPS) spectra were calibrated using the C1s peak at 284.8 eV as an internal reference. Background correction was performed using the Shirley method, and peak

deconvolution was carried out using a Gaussian–Lorentzian (GL) fitting function. The fitted peaks were assigned based on standard binding energy values reported in the literature [10] [11]. **Fig. 3 (b), (c) & (d)**, were analysed to confirm the membranes' chemical structures. PVA-induced peaks in the C1s envelope are attributed to the -C=O, -C=C-O (about 289 eV), -C-H, -C=C, and C-C (approx. 285 eV) moieties. C=O and C–O functional groups are represented by peaks at ~532 eV and ~530.2 eV in the O1s spectra, corresponding to carbonyl and hydroxyl functionalities associated with PVA and crosslinking interactions. [285]. Table 3.1. Summarizes the XPS parameters and all the binding energies for the fabricated membrane.

Table 3.1. Summary of XPS fitted parameter, binding energies and corresponding functional assignment for the fabricated membrane

Elements	Binding energy (eV)	Assignment	Literature range
C1s	~284.8	C-C/ C-H	284.6-285.0
C1s	~288.5	C=O/ O-C=O	287.5-289.0
O1s	~532.0	C-OH	531.5-533.0
O1s	~530.2	C=O/C-O	530.0-531.5

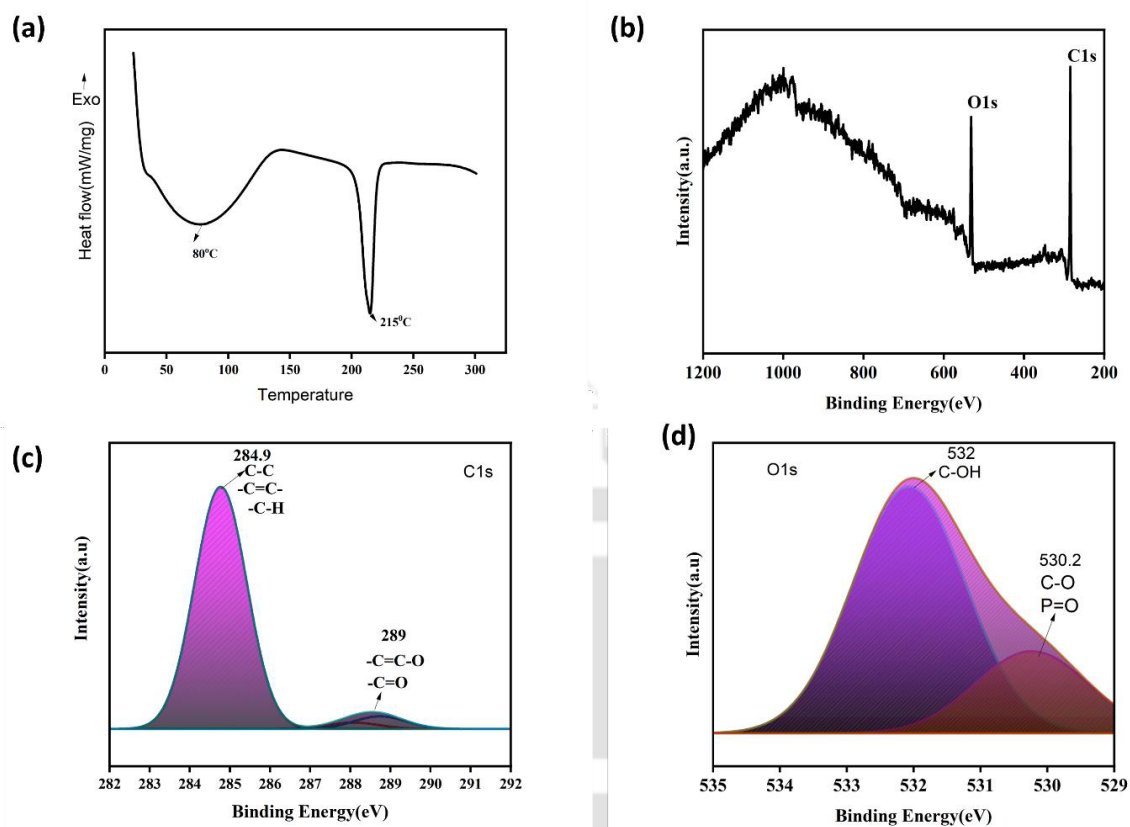


Figure 3.3. (a) DSC analysis of fabricated membrane, (b) XPS survey spectra of crosslinked fabricated membrane, (c) Deconvolution spectra C1s (d) Spectra of O1s

3.2.4. Surface morphology and wettability of the fabricated membrane

With a scan area of $10\ \mu\text{m} \times 10\ \mu\text{m}$, **Figure 3.4 (a)** displays 3D surface topographies obtained from AFM analysis to assess the impact of PVA-GA crosslinking on surface roughness. The images display surface peaks, or raised structures, in the brightest areas and valleys or pores in the darkest areas. The analysis also produces the mean surface roughness (R_a), which provides quantitative data on the membrane's topographical characteristics. The AFM analysis provides information on the surface morphology and roughness of the membrane. The surface roughness (R_a) of the pure PVA membrane was 22.65 nm. However, surface roughness does not directly determine the hydrophilicity of the material. The hydrophilic nature was determined from its chemical composition, where the presence of a hydroxyl group was found through FTIR

analysis. Thus, surface roughness plays a secondary role by influencing wettability. According to the Wenzel model, surface roughness amplifies the intrinsic wettability of the material by increasing the effective contact area between the liquid and surface [12]. which was comparatively smoother than the crosslinked membrane. Crosslinking with GA has resulted in an increase in the Ra value to 47.70 nm, due to formation of a three-dimensional crosslinked network in the polymer matrix, leading to structural rearrangement, localised aggregation and heterogeneity on the membrane surface. An examination of the water contact angle indicates that when the contact angle decreases, the membrane's hydrophilicity rises. The drop angle value shows how well the membrane and water bind together; specifically, a decreasing contact angle implies that the water molecules and membrane are more compatible because of the presence of polar groups. The PVA matrix's surface roughness is successfully increased by adding glutaraldehyde (GA), a crosslinking agent, as seen in **Figure 3.4. (b)**. The highest contact angle of the crosslinked PVA-GA membranes was 68.4° , while the contact angle of pure PVA membranes is approximately 41.4° . Crosslinking reduces the membrane's hydrophilia (**Figure 3.4. (c) & (d)**).

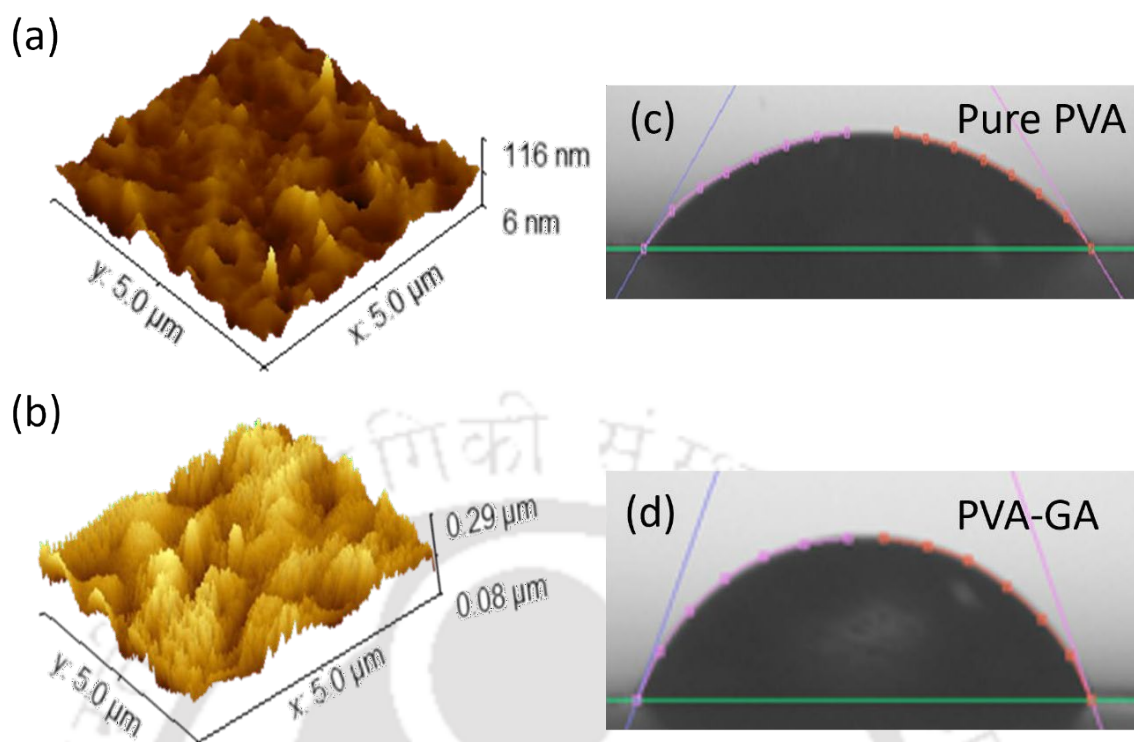


Figure 3. 4. Surface morphology and wettability study of both pure PVA and PVA-GA

3.2.5. Potentiometric response of mini DCMFC upon variable carbon content in analyte

The miniature MFC was inoculated with Real Municipal wastewater (RMW) with the help of a syringe through the tube of the MFC. Wastewater is collected once a week. The sample collected from the site was promptly refrigerated and stored until further use. To ensure a consistent flow of electricity, the pre-acclimation process is executed [3]. The system was equipped with an external load of $1\text{ K}\Omega$, such that it requires a shorter duration for biofilms to form. The acclimatization process for miniature MFC took a comparatively short period since it is smaller in configuration with reduced ohmic losses, and mass transport is quite improved between the small volume of wastewater biofilm and electrodes compared to large and medium-sized MFCs [286]. Also, in such a way that it takes a shorter duration to achieve better cell-electrode adherence. The voltage obtained during acclimation is shown in **Figure. 3.5(a)**. The cycle of biofilm growth on the electrode surface is completed when the voltage rises from

zero, peaks, and then starts to fall. This is referred to as the activation phase [287]. The variation in the recorded voltage indicates that the microorganisms got acclimatized in a miniature MFC setup fed with a small volume of RMW [288].

3.2.6. Effect of anolyte on MFC performance

The miniature MFC was replenished with RMW when the voltage reached baseline. It was observed that the pattern of voltage output remains the same without any precaution while refilling in anaerobic conditions. The temperature used throughout the whole procedure was 37°C, maintaining anaerobic conditions [289]. The enriched DCMFC was supplied with RMW at varying substrate concentrations (SC) from 0.5 to 1.5 g/l. **Figure 3.5 (b)** illustrates the potentiometric response of the mini DCMFC to changes in RMW SC concentration. Here we can observe three phases of the growth and charge transfer process. In the initial phase, bacteria metabolize the complex organic substrate, synthesize their necessary building blocks, and acquire other necessary elements required for their replication. However, there is no cell division at this stage. In the subsequent phase, bacterial cells start colonizing when all cell components like DNA, RNA [290], and other metabolic products are already generated, and thus, the initial production of electrons occurs. In the third phase, when available nutrients are consumed with time, the number of cells decreases, and waste accumulates. Bacterial growth reaches a plateau where there is no overall population growth [291]. Spore-forming bacteria may start forming endospores and some virulence factors, resulting in harsh survival conditions [292]. Consumption of primary electrons becomes equal to the generation of secondary electrons. And thus, the last phase is being equilibrated. The voltage on the other side increases straightaway with time, which is known to be the logarithmic phase of bacterial growth when bacterial cells increase in numbers. Excessive substrate concentration creates a niche for the growth of methanogens under a favourable environment [293]. When an adequate amount of biomass in

wastewater is formed, the use of exorbitant amounts is not necessary since there is an optimum threshold for the manifestation of the metabolic reaction rate of microorganisms residing in the electrode. Also, it is under sub-concentration that does not affect the OCV. A significant correlated relationship was noted between substrate concentration (SC, g/L) and voltage output within the range of 145 to 185 mV within the first hour, considering the anode's total area. The miniaturized environment contributed to faster cell-to-cell communication, facilitating substrate metabolism [294]. The subsequent phases involved bacterial colonization and electron production. The linear range defined non-saturating fuel conditions for the DCMFC. For acetate concentrations above 1 g/l, the voltage output was no longer influenced by fuel concentration, aligning with microbial community growth kinetics. Figure 3.5(b). demonstrates no detectable voltage increase for acetate concentrations exceeding 1 g/l. Excellent reproducibility was observed for mini DCMFC at a concentration level of substrate that is 1 g/l. The response time of the miniaturized DCMFC, defined as the duration to attain steady-state voltage, proved significantly shorter than other reported MFC-type BOD sensors [295]. The small-scale mini DCMFC exhibited a shorter response time (t_r) as shown in Table 3.2, attributed to system miniaturisation and low Reynolds numbers, approaching the Hydraulic Retention Time (HRT) [296].

Table 3.2. Comparison of mini MFC types according to configuration, anode volume, and response time

Configuration	Anode volume (cm ³)	t_r (hr)	Reference
Double chamber	20	1	[297]
Double chamber	25	0.50	[298]
Single chamber	2	0.04	[299]
Single chamber	12.5	0.66	[294]
Double chamber	2	0.08	This study

3.2.7. Influence of heavy metal on the cathode compartment

Miniatured MFC reported so far, usually, ferricyanide solution is used as catholyte [300]. The

current study aimed to determine how the energy output of a small MFC is affected by the concentration of the catholyte solution containing heavy metals. The miniature MFC was operated with a substrate concentration of 1g/l substrate at the anode, while heavy metal reduction upshot in the cathode compartment was examined, leading to low-level energy generation. **Figure 3.5(c)** illustrates the impact of varying concentrations of chromium (as potassium dichromate) on the performance of the MFC. The concentrations of the heavy metal test, specifically Cr^{6+} , were set at 30 mM, 50 mM, and 70 mM, allowing for the assessment of their influence on the cathode side by substituting potassium ferricyanide as the ⁷electron acceptor. this study was focused on investigating the results of adding Cr^{6+} on the cathode side by replacing potassium ferricyanide as the electron acceptor. The aim was to examine how this substitution influenced the system's performance. This approach was adopted due to the relatively high oxidation potential of Cr^{6+} (1.33V) compared to potassium hexacyanoferrate (0.36V). By utilizing chromium (VI) as the electron acceptor in the cathode, it was anticipated that the system could potentially exhibit improved performance. It was observed that a concentration of 50mM Cr^{6+} to be the optimum for better performance of MFC [301]. Since a steady rise in maximum voltage was observed with the concentration given. Perhaps the reason for this is the increased redox potential $\text{Cr}_2\text{O}_7^{2-}$. By increasing the catholyte concentration, there is no effect in bacterial metabolic rate in the anode compartment as the substrate concentration was kept constant throughout the process in real wastewater. A variety of techniques may be used to remove heavy metals from soil and wastewater, including chemical precipitation, ion exchange, biosorption, membrane filtration, bioremediation, and others. However, with their high rate of removal and ability to generate power, microbial fuel cells (MFCs) provide an affordable and sustainable substitute [91]. Despite this, there is limited research on heavy metal removal using micron-scale MFCs while simultaneously generating power. Here in this work,

we have used a double-chambered mini MFC for our preliminary study on lead as one of the heavy metal removal efficiencies from wastewater, which was fed to the anode chamber of the DCMFC (Table 3.3).

Table 3.3. Utilisation of microbial fuel for heavy metal removal cells (MFCs) in wastewater treatment

Metal	Anode volume (mL)	Fabrication of MFCs	Effective removal (%)	Optimal output (mW/cm ²)	Reference
Cu(II)	100	SCMFC-pt coated	98.3	10.2	[302]
Cr(VI)	340	Double chambered	12.72	1221.91	[303]
Cd(II)	12	SCMFC-Cc cloth	90	3.6	[304]
Hg (II)	120	Double - chambered carbon paper cathode	3.08	318.7	[305]
Ag(I)	112	Two-part MFC	99.91	4.25	[306]
Au (III)	72	Dual-chamber MFC	99.88	6.38	[307]

Pb (II)	2	Dual	24	13.85	This study
chamber					
without					
catalyst					
coating					

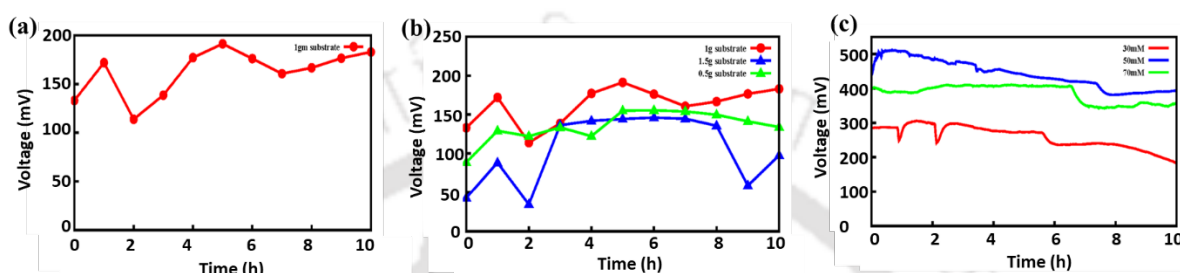


Fig.3.5. (a) Early acclimatisation reaction of RMW-supplied mini DCMFC, (b) performance evaluation under different SC, (c) Voltage output in relation to differing concentrations of potassium dichromate as catholyte

3.2.8. Bioelectricity production of biomimetic miniature MFC

Operating under the fed-batch mode and employing both Nafion-117 and PVA-GA membranes, stability in the investigated Microbial Fuel Cells (MFCs) was achieved after approximately two weeks. A consistent rise in voltage was observed under an external load of 1 K Ω , with no significant lag during start-up, indicating efficient microbial cell-to-anode adhesion. Upon attaining a stable potential, an assessment of sustainable power generation was conducted, involving an evaluation of how considerably the relative variation in anode potential (RDAP). To delve into the electron discharge characteristics of the biocatalyst, cyclic voltammetry (CV) was utilized with an Electrochemical analyzer (CHIE60 series). The cathode and anode served as the counter electrodes and working electrodes, respectively. In situ electrochemical experiments were performed in the DSW electrolyte, with an Ag/AgCl (S) reference electrode. Cyclic voltammetry (CV) was conducted by implementing a potential ramp on the working

electrode (anode) at a scan rate of 10 mV/s, spanning from +1 to -1 V. The in-situ evaluation of electron discharge by cyclic voltammetry (Vs Ag/AgCl (S)) over time facilitated a better understanding of alterations in metabolic pathways and electron transporters. The PVA-based MFC exhibited a sigmoidal voltametric response with redox peaks at 460 mV and -460 mV, indicating microbially mediated electron transfer processes governed by diffusion and kinetic limitations, as shown in **Figure 3.6 (a)**. This behaviour reflects the involvement of redox-active biomolecules and substrate-controlled electrochemical reaction. The crosslinked PVA-GA membrane demonstrated superior open-circuit voltage (OCV) and current density as indicated in **Table 3.4**. As illustrated in **Figure 3.7**, the columbic efficiency of the PVA-GA-based mini MFC was 85.5%. This is higher because the PVA-GA membrane, which is used as a separator and proton exchange membrane, is hydrophobic. Additionally, the flow channel is micron-scale and biomimetic, which results in improved fluid micromixing and a shorter electrode distance because of its sandwich arrangement. Also, because there is less diffusion of oxygen from the cathode to the anode and substrate from the anode to the cathode. The COD removal of PVA-GA was $68 \pm 0.10\%$ as shown in **Figure 3.6**. It is also due to the specialized structural configuration of the biomimetic MFC, which limits the aerobic degradation of the microbes due to decreased oxygen diffusion.

3.2.9. Internal resistance of mini DCMFC and substrate crossover study

In order to better understand the interface properties, electrochemical impedance spectroscopy (EIS) studies reveal the ion movement within the electrodes. The kinetic properties and electrode reactions collectively influence ion mobility. Material morphology plays a pivotal role in shaping these factors. Ion and electron transport mechanisms, along with charge transfer processes, are integral components determining the overall transport dynamics [308]. **Figure 3.5(b) and 3.5(c)** show the Graph showing the Nyquist curve for the ZsimpWin-fitted matching

circuit. To simulate the impedance characteristics of the polymer gel electrolyte and align with the measured impedance data, Modified Randles-type equivalent circuits $R(Q(R(QR)(Q(RW))))$ incorporating constant phase elements (CPE) and Warburg impedance are widely used to model non-ideal electrochemical behavior in biofilm-based systems, polymer electrolytes, and microbial fuel cells, where surface heterogeneity and diffusion-controlled processes play a significant role as seen in reported literature [17], [18], [19], [20]. The incorporation of constant phase element (CPE) and Warburg element in the modified Randles circuit is established in microbial fuel cell systems and polymer electrolyte systems to address surface heterogeneity and diffusion constraints. In the amalgamation of electrolyte and polymer, the first part represents the bulk resistance (R_s). The electrolyte resistance (R_1) and a constant phase element (Q) are combined in parallel in the second component. A series connection to electrolyte resistance (R_1) is established by connecting a constant phase element (Q) in parallel with the polymer gel electrolyte's charge transfer resistance (R_{ct}) and Warburg impedance (W) [309]. Parameters R_s and R_{ct} are examined in the EIS spectra [310]. The values of R_s , R_{ct} , and W for both kinds of mini DCMFCs are listed in **Table 3.5** below. The presence of sulphonic acid groups in its polymer chain is the main reason why the Nafion-based DCMFC exhibits less solution resistance than the crosslinked membrane [311]. Even though PVA is an insulating substance without polar groups [312]. Comparing the PVA-GA-based micro DCMFC to the Nafion-based DCMFC, we find that the former has a reduced charge transfer resistance. Establishing a significant current draw is necessary to extract electrical energy from fuel cell activity, but the fuel cell's intrinsic irreversible losses reduce the real cell potential [89]. The total conversion efficiency is reduced due to the many forms of losses that obstruct the electron movement from the anode to the biocatalyst. Activation losses, caused by the rates of bio-electrochemical reactions at the surface of the electrode, diminish with an increase in electron flow inside the circuit [313]. Electrons generated by substrate degradation have

activation losses as they travel passing via the biocatalyst, the anode, and finally the cathode, due to impediments they encounter [293]. The activation barriers that the responding species or biocatalyst must overcome in biochemical and bio-electrochemical processes are very comparable. The current density was calculated by normalising the measured current with respect to the effective electrode surface area. Due to the miniature configuration of the MFC and the small electrode area, the normalised current density appears comparatively high. Therefore, the reported value represents the apparent current density in the context of a micron-scale microbial fuel cell system where,

$$i = I/A$$

The exchange current density of the mini DCMFC post-augmentation was measured at 1.2 A/cm². The exchange rate between reactants and products reaching a state of balance is represented by this value. Testing acetate diffusion in the lab-fabricated crosslinked PVA membrane-based mini DCMFC was crucial due to a viable anode-to-cathode fuel crossover chamber, impacting MFC performance [318]. The diffusion of a set quantity of acetate to the cathode chamber was measured, using the methodology described in an earlier article [312]. **Table 3.4** provides a summary of the membrane type, anode material surface area, volume, and substrate crossover study in the miniaturized DCMFC.

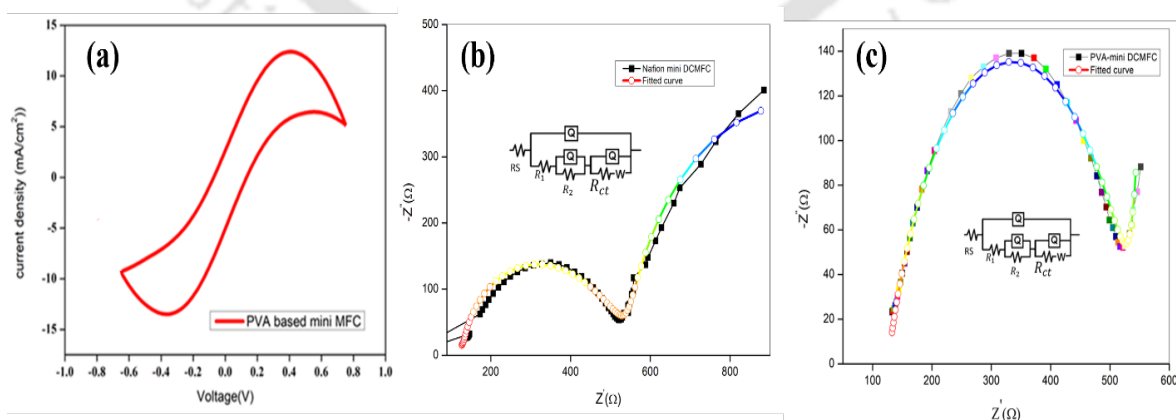


Figure 3.5. Biomimetic mini MFC electricity production (a) Cyclic voltammetry, PVA-GA-based mini MFC (b) Nyquist plot of Nafion-based MFC (c) PVA-GA-based MFC

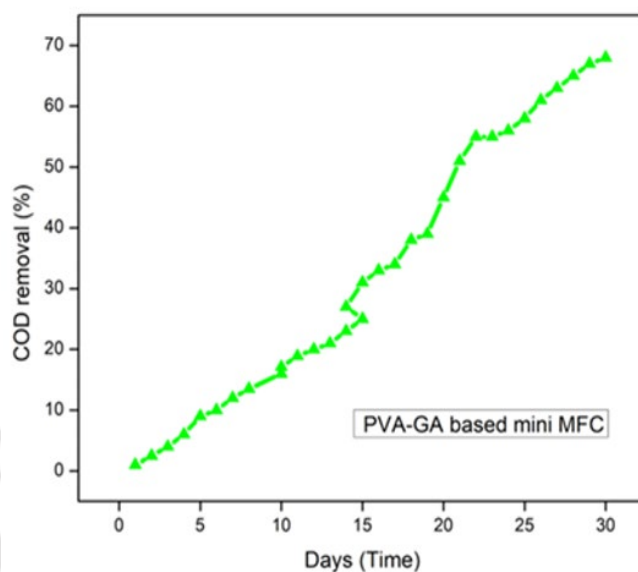


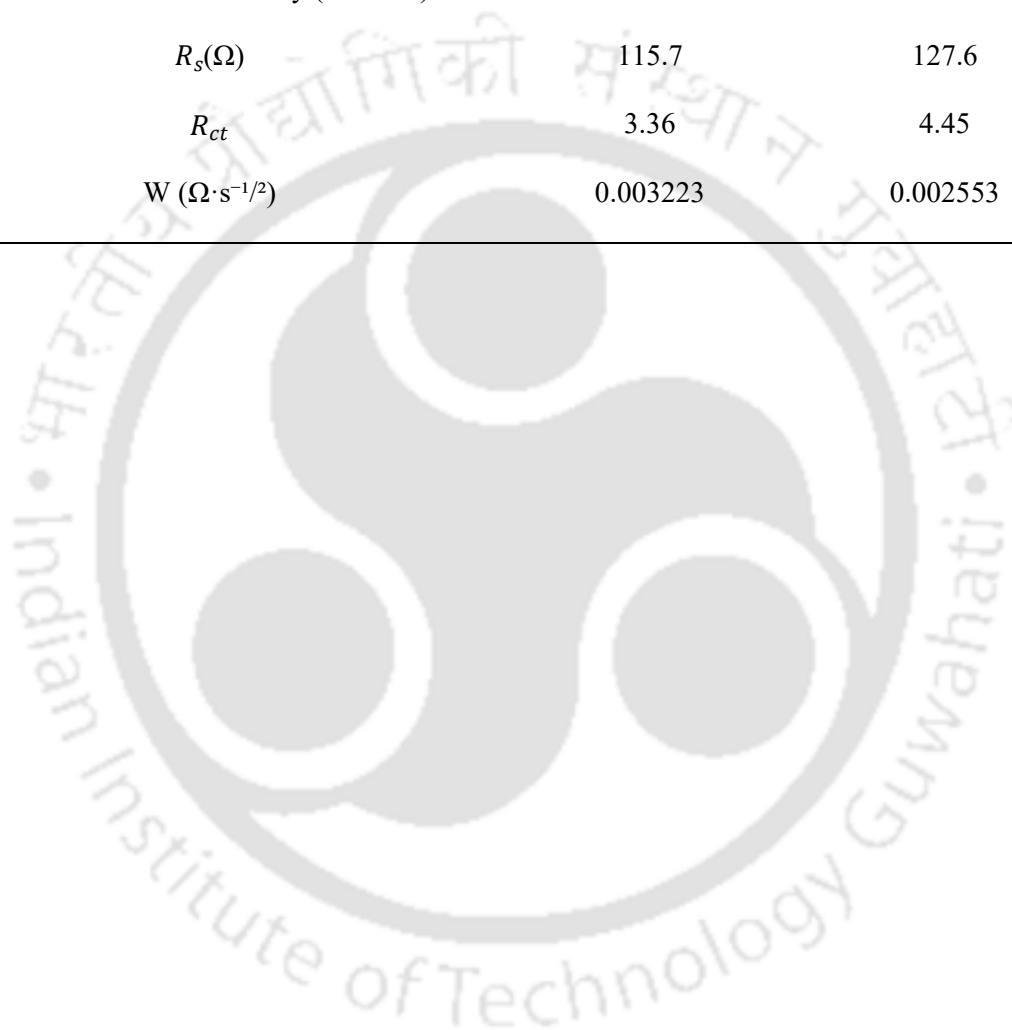
Figure 3.6. COD removal by crosslinked PVA-based Mini DCMFC

Table 3.4. Summary of types of membrane used in miniature MFCs according to their anode volume, surface area, the external substrate used, and their crossover study

Anode chamber (mL)	Inoculum	Conductive Anode material	PEM	Surface domain (cm ²)	substrate	Substrate cross-over Diffusivity (Dcm ² /sec)	Ref.
2.5	Mixed bacterial culture	Carbon cloth	Mediator or less	7	Acetate	NA	[1]
1.2	<i>Shewanella oneidensis</i> DSP-10	Graphite felt	Nafion-117	2	Lactate	NA	[2]
0.65	<i>S. oneidensis</i> MR-1	Gold	Nafion-117	0.385	TSB	NA	[3]
0.4	<i>S. oneidensis</i> MR-1	Graphite felt	Nafion-117	25	Lactate	NA	[4]
0.016	<i>Saccharomyces cerevisiae</i>	Gold	Nafion-117	0.51	Glucose	NA	[5]
2	Mixed Bacterial culture	Graphite felt	PVA-GA	4	Acetate	0.008395×10^{-6}	This study

Table 3.5. Properties of mini DCMFC equipped with Nafion and lab-fabricated PVA membrane

Membrane	PVA-GA based DCMFC	Nafion-based DCMFC
Maximum open circuit potential (mV)	723±0.3	659±0.7
Highest Columbic efficiency (%)	85.5	79.7
Maximum Current Density (mA/cm ²)	13.85	16.15
$R_s(\Omega)$	115.7	127.6
R_{ct}	3.36	4.45
$W (\Omega \cdot s^{-1/2})$	0.003223	0.002553



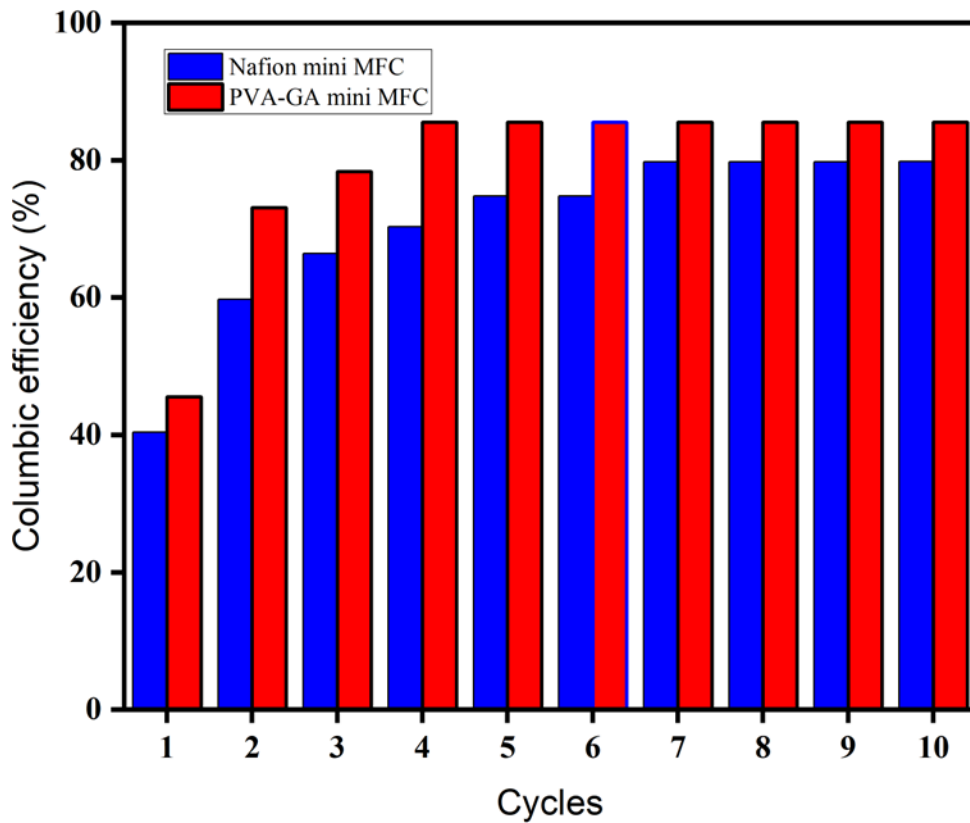


Figure 3.7. Coulombic efficiency of PVA-GA and Nafion-based mini MFC

3.2.10. Biofilm Analysis

The biofilm's dynamic behavior profoundly influences power generation[323]. In **Figure 3.8**, the biofilm that has developed on the anode electrode is seen in a morphological perspective. When the electrode made of graphite felt and the biofilm layer thereon is examined more closely, various forms of bacteria are observed, including round-shaped and rod-shaped bacteria, with the majority being present in these forms. The microbial flora exhibits a diverse range of structures, ranging from minute to substantial, with some bacteria measuring below $1\mu\text{m}$ in size. Symbiotic attachment among the microbial flora is facilitated by hair-like projections known as pili, which are essential for creating a strong biofilm matrix on the anode surface [313][324] and in the movement of electrons from organisms to the area that serves as the anode. Experimental findings highlight the biocompatible nature of the electrode with

bacterial cells. The microenvironment of the mini MFC provides an adequate site for microbial attachment, resulting in enhanced performance of the crosslinked PVA-based miniature MFC. When real wastewater, containing complex macromolecules such as polysaccharides, is utilized in miniature MFCs, electrogenesis is observed.

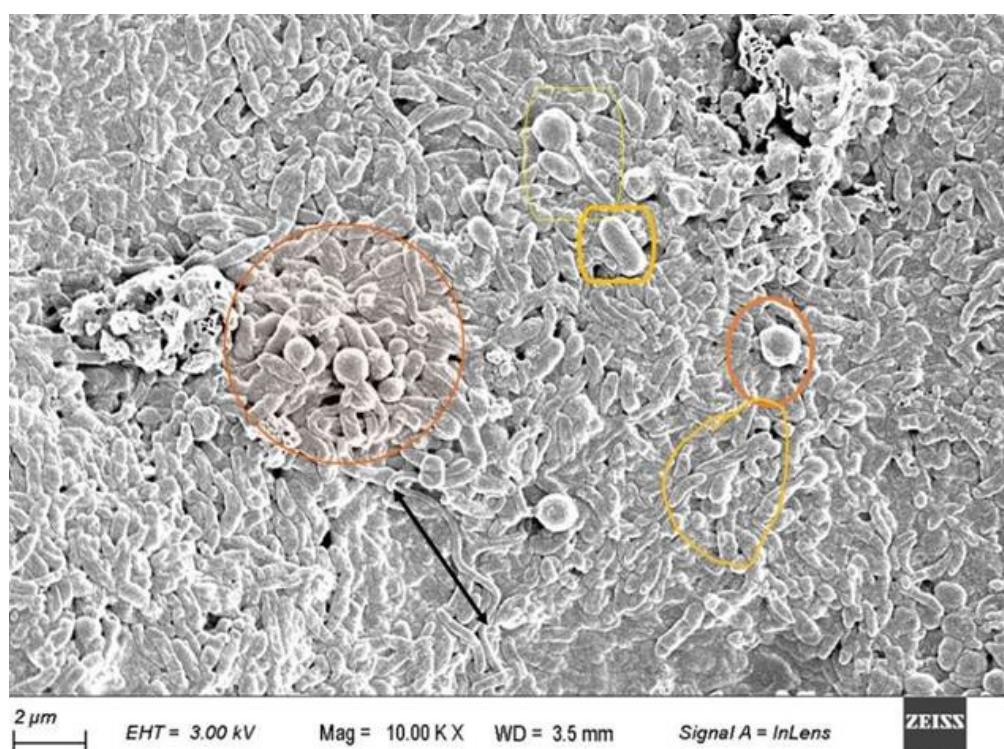


Figure3.8. Bacterial Biofilm layer with conductive pili on the electrode surface

3.2.11. Cost analysis

Microbiological fuel cells (MFCs) reduce overall energy usage and waste disposal costs by converting waste into power. The effective scale-up of MFC technology relies on the optimization of system costs, including membrane selection and monitoring components. Wastewater characteristics, organic loading rates, operating conditions (pH, temperature, cycle duration), microbial acclimation, and operational scale all have an impact on the operational expenses of MFCs. The efficiency of membrane technology in terms of cost is crucial in assessing the viability of MFCs for industrial applications. Commercial polymeric membranes used in extensive processes often cost between \$50 and \$200 per square meter [325]. In place of the more expensive Nafion 117 membrane, this study developed a separator based on

laboratory-synthesized crosslinked PVA which was priced at ₹25,993.39 per 900 cm². The overall manufacturing cost of the crosslinked membrane was calculated based on expenditures for raw materials, power use, and labour charges [326] as **tabulated 3.6(a)**. Equipment, power requirements, operation time, and energy pricing all contribute to total electricity consumption cost.

It is calculated using an equation,

$$C_e = P * n * t$$

In which C_e represents the electricity consumption cost, P denotes the equipment's power consumption (in kW), n refers to the number of operating hours, and t indicates the electricity price.

The synthesis procedure used 4 kWh of power, whereas annealing necessitated an extra 5.5 kWh, at a tariff cost of ₹5.96/kWh. worker costs were determined using a skilled worker pay of ₹954 (11.12 USD) per day (according to the Ministry of Labour & Employment, India) [327], with an extra 20% designated for laboratory expenditures. The ultimate expense of the crosslinked membrane amounted to ₹3,954.68/ft² (1 USD = 85.76 INR), making it eight times more economical than Nafion 117 (₹26,831.84/ft²), thus presenting a feasible and cost-efficient option for MFC applications. Alongside the lowering of membrane costs, a cost-effective and efficient monitoring system is crucial for the assessment of MFC performance. Although commercial multimeters can quantify voltage in MFC studies, they provide many financial drawbacks. Advanced multimeters equipped with data recording features, such as the Fluke 289 True-RMS Standalone recording Multimeter, are priced at ₹1,45,950, making them excessively costly. Moreover, most commercial multimeters do not possess automatic recording capabilities, necessitating manual readings that elevate labour expenses and heighten the potential for human error. These devices have scalability limitations, since they can measure only one MFC at a time, requiring numerous units for concurrent multi-channel

monitoring, hence increasing expenses. A low-cost smart data recorder was created to address these difficulties, using an Arduino UNO-based system that includes four single-ended input channels, a 16-bit I2C ADC with a four-channel programmable gain amplifier module, a voltage range of 2V to 5V, and an ADC converter with a display module as listed in **Table 3.6(b)**. This configuration provides an economical alternative to commercial multimeters, enabling automatic, continuous voltage monitoring and real-time performance evaluation of MFCs. This work effectively lowers the capital expenses related to MFC operation by creating a lab-engineered crosslinked separator and an Arduino-based intelligent data logger. The crosslinked membrane is eight times less expensive than Nafion 117, whilst the Arduino-based monitoring device offers a cost-effective substitute for costly commercial multimeters. In light of this technique, MFCs are now more economically feasible for treating wastewater and producing bioelectricity, facilitating scalable and sustainable implementation in both industrial and decentralized settings.

Table 3.6(a) Cost analysis of the lab-fabricated crosslinked PVA utilized in mini DCMFC

Components	Quantity used	Price/ft² USD (1 USD = 85.76 INR)	Price/ft² USD (1 USD = 85.76 INR)
Polyvinyl Alcohol Sigma Aldrich	2g	0.50	1.01
Glutaraldehyde Finar	0.51	6.29	3.21
Labor, Power, and Other Expenses in Membrane Casting	--	--	41.87
Total	--	--	46.10
Nafion-117 Sigma Aldrich	--	--	312.87

Table 3.6 (b) Cost Analysis of Smart Data Logger vs. Commercial Multimeter used in MFC experiment

Components	Model	Quantity	Unit Price/USD
ESP32 Development Board with WiFi and Bluetooth	EC-2608	1	4.60
ADS1115 16-Bit 12C ADC 4 -4-channel programmable Gain Amplifier Module	EC-3214	1	5.58
2.44 cm (0.96 inches) OLED Display Module	Ec-2981	1	3.90
GL12840 Points Solderless Breadboard	EC-0160	1	0.37
Alligator clips-Double ended crocodile	EC- 8023	1	0.27
Total			14.75
Fluke 289 True-RMS Stand-Alone Logging Multimeter			1701.84

3.3. Conclusions

A significant improvement over conventional large-scale microbial fuel cell (MFC) systems has been the development of a portable, compact Microbial Fuel Cell (MFC), which offers a cost-effective and scalable alternative for wastewater treatment and bioelectricity production. By combining a specialized microfluidic flow channel with a cheap, lab-fabricated PVA-based separator, the mini-MFC is more feasible and economical than conventional setups that require significant space, costly Nafion-117 membranes, and external catalysts. Its catalyst-free functioning makes it much more feasible for practical use, especially in environments with restricted resources. While retaining COD removal effectiveness equivalent to bigger systems, the modified microfluidic flow channel enhanced microbial activity, enabling effective organic matter breakdown and energy production. It has been found experimentally that the micro MFC's PVA-based separator produced a current density of 13.85 mA/cm², coulombic efficiency of 85.5%, indicating its great potential for energy production. Furthermore, the system's COD removal efficiency of 68±0.10% demonstrated its effectiveness in treating wastewater. Additionally, a preliminary evaluation of Pb(II) removal was done with 24% reduction, suggesting mini-MFC potential for concurrent bioelectricity generation and heavy metal

reduction. Despite being early, these results suggest that lead removal effectiveness may be further improved by optimising electrode materials and operating conditions. The system's monitoring capabilities were further enhanced by the addition of a multi-channel Arduino-based smart data recording system, which offered precise real-time voltage tracking at a far lower cost than commercial equivalents. Modular arrays might improve this technology's scalability for decentralized energy production and wastewater treatment. All things considered, this small MFC system's price, mobility, and efficiency make it a strong contender for environmentally friendly applications. Furthermore, compared to other macron and micron-sized MFCs utilised for energy production that have been documented in the literature, the cost is also lower. One of the main bottlenecks in the current generation using MFC technology is the cost, which is reduced eightfold when using a PVA-GA lab-fabricated membrane as an alternative. This cost is further reduced when using lab-fabricated data logging devices instead of commercial data loggers. To optimize COD and heavy metal removal efficiency under practical circumstances, future studies should concentrate on enhancing power management systems, optimizing the separator material, and scaling up the technology.



Chapter-4

Eco-Engineered N-Methyl-2-pyrrolidone-Free Antibacterial Chitosan/Cellulose Acetate membrane Separator for Real Hospital wastewater-fed Microbial Fuel cells

Motivation

The escalating release of untreated hospital wastewater, which harbours pathogenic microorganisms, antibiotics, and hazardous organic pollutants, presents a substantial risk to both environmental integrity and public well-being. Microbial fuel cells (MFCs) present a potentially effective approach, enabling simultaneous wastewater treatment and energy generation however, their efficacy is frequently compromised by membrane fouling, biofilm instability, and the employment of toxic solvents in membrane production. Traditional membrane processing, which utilises N-methyl-2-pyrrolidone (NMP), raises considerable environmental and health issues, thereby necessitating the creation of safer and more environmentally friendly alternatives.

The work in this chapter is published as

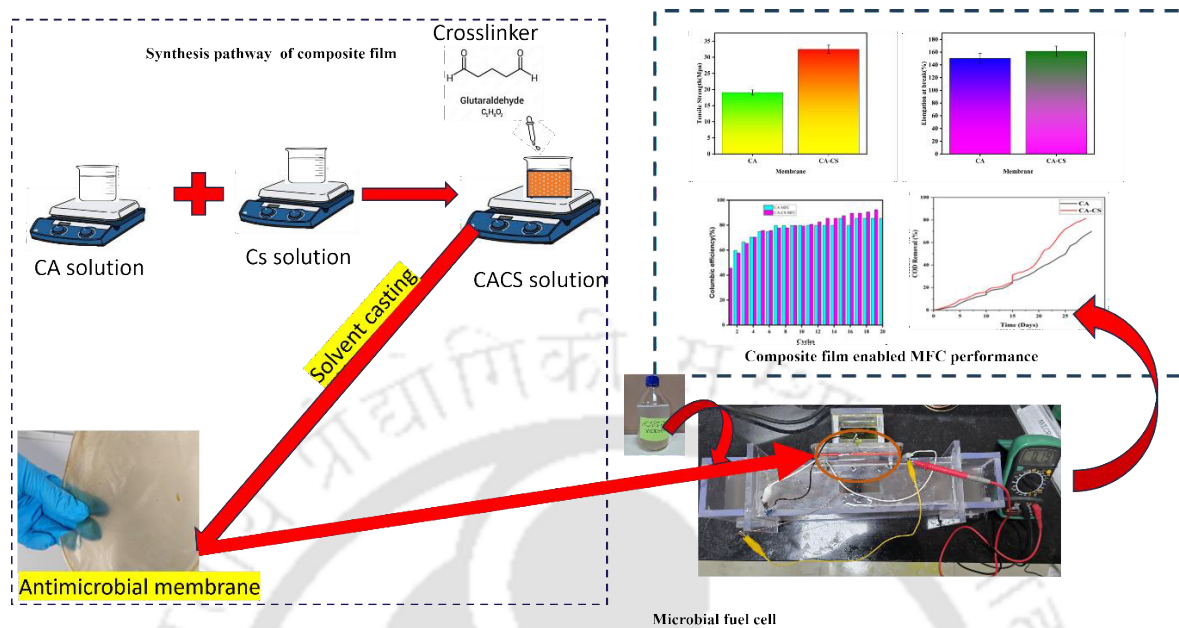
Aparajita Roy, Sonu Kumar, Bhanupriya Das, Kuhelika Das, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, Eco-engineered N-Methyl-2-pyrrolidone-free antibacterial chitosan/cellulose acetate membrane separator for real hospital wastewater-fed microbial fuel cells, Next Research, Volume 2, Issue 4, 2025, 100867, ISSN 3050-4759,

<https://doi.org/10.1016/j.nexres.2025.100867>.

Abstract

This chapter focuses on the utilisation of hospital wastewater, comprising a complex amalgamation of pharmacologically active substances and toxic contaminants, presenting threats to ecosystems and human health. Inadequate treatment may result in water contamination and the spread of infectious illnesses. Microbial Fuel Cells (MFCs) provide an efficient method for treating HWW by utilizing organic-rich contaminants as substrate while producing bioelectricity. The present study produced a cost-effective, environmentally friendly bio-composite membrane composed of cellulose acetate (CA) and chitosan (CS) as an alternative to PFAS-based membranes such as Nafion. The CA-CS membrane was synthesised using glutaraldehyde (GA) crosslinking, which reduced free hydroxyl groups and established ether and acetal connections, therefore improving chemical and mechanical stability. The membrane demonstrated superior physicochemical characteristics, with a tensile strength of 32.47 ± 1.30 MPa and an elongation at break of $161.47 \pm 8.07\%$, hence assuring durability under operational stress and resistance to biofouling. Electrochemical Impedance Spectroscopy (EIS) demonstrated a minimal charge transfer resistance of 3.8Ω , resulting in a substantial exchange current density of 1.2 mA/m^2 , signifying effective electron transfer and catalytic performance. In hospital wastewater-fed MFCs, the CA-CS membrane attained a Coulombic efficiency of 92.18% and a COD removal efficiency of $83.4 \pm 0.10\%$. The membrane production procedure used water as a solvent, so removing harmful chemicals and activation stages, thereby promoting green synthesis. A techno-economic study calculated the manufacturing cost at 45.62 USD/ft², making it 6.87 times more cost-efficient than Nafion-based membranes. This environmentally sustainable and cost-effective membrane provides a viable alternative for real-field HWW treatment and renewable energy production.

Graphical Abstract



4.1. Introduction

The main goal of waste management is to reduce the negative effects of garbage on the environment and public health. Hospital wastewaters (HWW) exhibit qualitative similarities to municipal wastewaters; nonetheless, they include harmful and infectious chemicals and compounds that pose risks to environmental health, the safety of personnel in these facilities, and the broader community. Hospital effluents include various substances used in medical, laboratory, and research applications, together with human excreta. This includes both insoluble and soluble organic and inorganic pollutants, which are very harmful to people and aquatic organisms even at minimal doses, and are categorised as biologically active chemicals. Furthermore, HWW retains residual low-grade heat from pharmaceutical processes, which may be used to enhance microbial activity and increase the ionic conductivity of the MFC's membrane, hence optimising system performance [318]. Hospital wastewater (HWW) is generally released into Wastewater Treatment Plants (WWTPs) and co-treated with urban wastewater (UWW) in the majority of nations. Nonetheless, the principal physico-chemical properties of HWW often exceed those of UWW[319] [320]. Hospital effluents can be five to fifteen times more harmful than urban effluents, according to studies, and they may even prevent activated sludge operations in wastewater treatment facilities [321]. Therefore, in order to protect the public's health, it has been stressed in recent years that all hospitals, medical facilities, and health centres should have a facility for treating the wastewater they create. Because hospital wastewater contains both organic pollutants and newly discovered toxins such as per- and perfluoroalkyl substances (PFAS), treatment is essential, especially when it comes to safety and regulatory concerns [276] [322]. Notwithstanding the increasing interest in sustainable wastewater treatment technologies, a significant deficiency persists in the use of economical composite membranes for hospital wastewater treatment using microbial fuel cells (MFCs). Traditional membranes, such as Nafion, although efficient, are excessively costly and raise environmental concerns due to PFAS concentration, while bio-based alternatives often

encounter challenges related to stability, proton conductivity, and fouling resistance. Confronting this problem requires the development of sustainable, high-performance composite membranes that can simultaneously enhance energy recovery and pollutant removal from complex effluents, such as hospital wastewater. Membrane fouling denotes the deposition and buildup of undesirable substances on the membrane surface or inside its pores, significantly diminishing operational performance. Biological fouling arises from the adhesion and proliferation of microorganisms, resulting in biofilm development that gradually impairs membrane performance during forward osmosis (FO) operation [323][324]. Traditional wastewater treatment and water reclamation methods are typically inadequate in fully eradicating PFAS. Although their concentrations in the natural environment are typically modest, some wastewater treatment methods may cause PFAS buildup, leading to markedly increased levels [325]. An ideal forward osmosis membrane allows just water molecules to pass through while keeping solutes in their designated compartments; nevertheless, in actual applications, its selectivity is not perfect. To safeguard the environment and public health, regulatory frameworks established by the U.S. Environmental Protection Agency (EPA) and European Union (EU) directives are increasingly focused on the surveillance and reduction of biohazards, pharmaceutical residues, and per- and polyfluoroalkyl substances (PFAS) in wastewater [326][327]. Microbial Fuel Cells (MFCs) provide a novel approach for the treatment of hospital wastewater (HWW) by using its organic contaminants as a substrate for bioelectrochemical processes. Electrogenic microorganisms at the anode biodegrade these pollutants, simultaneously generating bioelectricity, reducing chemical oxygen demand (COD), lowering contaminant concentrations, and decreasing salinity. This process enhances the efficiency of subsequent filtration stages, making MFCs a sustainable and effective substitute for conventional HWW therapeutic modalities. To address these restrictions, this work employs microbial fuel cells (MECs) as a sustainable, cost-effective option. These

devices use microbial biofilm and extracellular polymeric substances (EPS) formed at the anode electrode surface as a result of wastewater presence. Current research on the use of microbial fuel Cells for treating hospital wastewater (HWW) is virtually non-existent, as studies have primarily concentrated on less complex wastewater categories like municipal wastewater or industrial discharges, with little attention given to HWW. MFCs offer significant advantages for HWW treatment, including the ability to operate across a wide range of temperatures, the use of mixed culture bacteria as biocatalysts, and the capacity to process diverse wastewater types as feedstock [328][329]. Microbial fuel cell (MFC) use aligns with Sustainable Development Goal 12, which emphasizes responsible production and use. MFCs reduce environmental impact and encourage sustainable practices by turning trash into a valuable resource by using organic waste and wastewater as substrates for energy generation [330]. This creative method helps create cleaner energy alternatives in addition to solving waste management issues. By recovering nutrients and bioenergy from waste streams, lowering reliance on outside energy sources, and reducing waste disposal difficulties, microbial fuel cells are essential to sustainable waste management. By efficiently treating wastewater, they reduce pollutants in the environment and encourage environmentally friendly production, which lessens the ecological impact of waste systems. Using MFCs to move from a linear economy powered by fossil fuels to a circular economy powered by renewable energy offers a revolutionary way to address pressing environmental issues, including climate change, the greenhouse effect, and global warming. In order to preserve terrestrial ecosystems and biodiversity, SDG 15: Life on Land places a strong emphasis on sustainable practices. By processing organic waste and pollutants in wastewater, microbial fuel cells (MFCs) help keep dangerous compounds from contaminating and deteriorating soil ecosystems. This strategy promotes the preservation of land-based habitats and preserves the health of the soil. By converting treated waste and nutrients into environmentally acceptable fertilizers, microbial

fuel cells (MFCs) reduce reliance on chemical substitutes that are detrimental to soil health and advance sustainability. MFCs help preserve forests and biodiversity by reducing the need for wood-based fuels and producing bioenergy from waste. Sustainable development is predicated on social responsibility, environmental preservation, and balanced economic growth. SDG 7 is one of the 17 Sustainable Development Goals (SDGs) set forward by the UN. By safeguarding universal access to affordable, sustainable, clean energy, it tackles significant issues for people, the environment, and global economic progress.

Long-term, "maintenance-free" monitoring may be possible with continuous sensor data transmission. A steady energy supply is necessary for frequent data transmission (e.g., every second or minute), yet power outages might make this source unstable. (Sustainable technologies, such as microbial fuel cells, inherently link energy generation and water treatment. MFCs clean water and generate power by utilizing organic debris in wastewater as a substrate for microorganisms' metabolism. Since two-chamber configurations have been the main focus of current research on MFC for water toxicants, there is still an opportunity for improvements in overcoming these energy and design constraints. Nonetheless, in spite of the encouraging potential of microbial fuel cells (MFCs) in hospital-derived wastewater (HDWW) treatment, the scalability and real-world application of these systems are significantly hindered by the lack of economically viable and environmentally sustainable membrane materials. Commercial PFAS membranes, such as Nafion®, while effective, are cost-prohibitive and derived from perfluorinated compounds known for their persistence and environmental toxicity[331] [332]. This high cost contributes to nearly 50–65% of the total MFC setup expense, thereby restricting large-scale deployment [333]. Moreover, membrane fouling and reduced proton conductivity over time further diminish system performance. Thus, the development of alternative low-cost, biodegradable membranes with comparable or improved ion transport and antifouling properties remains a critical research need to realize the full

potential of MFCs for decentralized wastewater treatment. A major obstacle to microbial fuel cells' widespread application is the exorbitant cost of the Nafion membrane, with Nafion-117 costing about \$33 for a 10×10 cm sheet [334]. Nafion is classified as a per- and polyfluoroalkyl substance (PFAS), which raises environmental issues owing to its persistence and probable toxicity. Moreover, the activation of Nafion generally necessitates the use of aggressive and corrosive substances, like hydrogen peroxide and sulphuric acid, therefore increasing environmental and operational challenges [335]. Recent studies highlight gaps in research on the efficient treatment of organic pollutants and new contaminants, including per- and polyfluoroalkyl substances (PFAS), found in hospital-derived wastewater (HDWW). Addressing these difficulties requires the creation of new materials that provide enhanced chemical resistance and selective permeability. There are several naturally occurring, hydrophilic, biodegradable substances with a large number of hydroxyl groups, cellulose, chitosan, and other polysaccharides, that are perfect for membrane applications to replace the use of expensive, biofouling, and toxic chemical compositions [336] [337]. Cellulose acetate (CA) has garnered significant scientific interest due to its inherent hydrophilicity, biodegradability, and ease of functionalization with various chemical groups to tailor its properties for specific applications [338]. Excellent mechanical and chemical durability, high hydrophilicity that makes them perfect for desalination, superior transport qualities, minimal protein adsorption, high water affinity, excellent film-forming ability, and affordability and accessibility are all features of cellulose acetate (CA) membranes. Gas separation has been accomplished using CA [339], reverse osmosis, microfiltration, and ultrafiltration techniques [340]. However, CA has a number of drawbacks, such as a limited pH and temperature operating range. Furthermore, the phase inversion preparation of the CA membrane produces an enormously dense skin layer and reduces the porosity of the porous sub-layer, resulting in an exceptionally low flux. The diffusion of the solvent and coagulant is much slower than that

of hydrophobic membranes. Some researchers modified CA membranes using various solvents, including N, N-dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP), and a mixed solvent made of N and N-dimethylformamide (DMF), in order to address these issues [341]. N-Methyl-2-pyrrolidone (NMP) and Dimethylformamide (DMF) are extensively used solvents in the production of cellulose acetate (CA) membranes owing to their robust solvating properties. However, both solvents are categorized as dangerous substances. NMP is recognized for inducing reproductive toxicity, dermal and ocular irritation, as well as respiratory complications upon inhalation. DMF is a recognized reproductive toxin and potential carcinogen, known to induce liver damage with chronic exposure and readily absorbed via the skin. From an environmental perspective, these solvents are not easily biodegradable and remain in aquatic and terrestrial ecosystems, presenting enduring ecological risks. They demonstrate water toxicity and possess the ability to bioaccumulate, hence affecting aquatic ecosystems. Modifications to CA membranes are often necessary to provide enhanced selectivity and increased flow [352]. Chitosan, due to its distinctive physicochemical qualities and adaptable composition and structure, presents several options for enhancing its use in water treatment. Chitosan may be efficiently modified via different physical and chemical processes to improve its efficacy in removing diverse pollutants from water sources. However, the high-water absorption and limited ion exchange capacity of pure chitosan limit its usage. By reacting with the amine and hydroxyl groups in its structure, crosslinking improves these restrictions. The motivation of this work is to develop an economical, crosslinked cellulose acetate–chitosan (CA–CS) composite film and assess its viability as PEM in microbial fuel cells (MFCs) for bioelectricity production using actual hospital-derived wastewater as the anolyte. The GA-crosslinked CA–CS membrane was methodically evaluated as a sustainable substitute for commercial PFAS-based membranes. Comparative assessments concentrated on essential parameters such as physicochemical properties, swelling behaviour for prolonged stability,

antifouling efficacy, mechanical strength, internal resistance, COD removal efficiency, bio-electrochemical output, heavy metal removal capacity, and overall cost-effectiveness to determine its viability for practical MFC applications.

4.2. Results and Discussion

4.2.1. Physicochemical properties of the crosslinked composite membrane

The FTIR investigation is a vital approach for a qualitative analysis of the produced materials. **Figure 4.1 (a)**. The FTIR spectra of CA and the CA-CS composite film, where the interaction between the CA and CS polymers occurred, are displayed. This was made clear by the notable variation in how new peaks appeared and how old peaks shifted. Similar spectral properties are displayed by the CA film and CA-CS composite films, with the O-H bond's stretching vibration peak located at 3538 cm^{-1} . The number of amine groups increases with the amount of CS, indicating its integration into the CA matrix and facilitating its interaction with the O-H group [353]. The characteristic absorption band due to the coincident ester-carbonyls (acetyl groups) in cellulose acetate is represented by the shifting of the adsorption band with the water absorption peak at about 1735 cm^{-1} . However, the carbon-hydrogen bonding (C-H) and carbon-hydrogen deformation in cellulose acetate are responsible for the displacement of the absorption band seen at about 2946 cm^{-1} . The stretching vibration peak of $-\text{CH}_3$ in the acetyl group corresponds to 1361 cm^{-1} [354]. In the composite, chitosan and cellulose formed a hydrogen bond. Strong C-O stretching of 1043 cm^{-1} is ascribed to both the glutaraldehyde crosslinker and cellulose. However, when compared to cellulose and chitosan alone, the hydroxyl peak's intensity dropped in the chitosan–cellulose composite beads. XRD spectrum of the samples as shown in **Figure 4.1(b)**, where CA exhibited two strong peaks at $\sim 8.38^\circ$ and $\sim 23.8^\circ$ and a relatively weak peak at $\sim 17.7^\circ$, whereas CA-CS showed characteristic peaks. The projections for the strong CA peak were at (1 0 0) and (0,0,2). When chitosan (CS) is added to

the composite film (CS-CA), the diffraction peaks at $2\theta = 21.02^\circ$ and $\sim 27.56^\circ$ with the crystal plane at (1 1 0) and (0,2,0) show a decrease in intensity as the chitosan content increases. This suggests a change in the original crystalline structure, which can be attributed to the strong interaction between CA and chitosan (Ravikumar & Sagadevan, 2021) [355]. Furthermore, when the chitosan content increased, the overall composite film's crystallinity reduced. This suggests that the molecular orientation of CA was disrupted and that the majority of the crystalline material had turned amorphous, improving the film's mechanical and flexible qualities. The diffraction patterns are different after copolymerization. In samples, the first peak from the (-110) plane should theoretically be at $2\theta = 12.5^\circ$. However, we only saw a fairly broad peak at about 14° in this investigation. If that were true, we would have also seen a peak at $2\theta = 22.5^\circ$, but that wasn't the case. Two lesser peaks were seen at $2\theta = 20^\circ$ and $2\theta = 22^\circ$ after the crystalline peak at $2\theta = 23.8^\circ$ vanished. The lattice planes (110) and (200) or (020) were the origins of these peaks. A similar pattern has been observed in Saini et al. [356]. This demonstrates the creation of CA-CS and demonstrates that the conversion of CA into CA-CS was made possible by the use of glutaraldehyde solution. The decrease in the degree of crystallinity is an additional factor, in addition to the polymorphic conversion that takes place throughout the polymerization process. This is because some crystalline regions have changed into amorphous ones. The study's findings also indicate that copolymerization contributed to a certain decrease in the degree of crystallinity. The polymorphic conversion of CA was confirmed by X-ray examinations, which made it possible to analyse the impact of the crystal structure of CA-CS on the effectiveness of metal ion removal in the following step. This effect has not yet been examined.

From the Sem image as shown in **Figure 4.2**, it can be deduced that both membranes exhibited a smooth surface with some small voids on the surface. This small void may be due to the evaporation of solvent during the drying of the film. Relatively CA-CS film appeared rougher

than the CA membrane. This observation is similarly supported by AFM analysis. A similar result has been reported by Zhang et al. [357]. Elemental screening using energy dispersive X-ray (EDX) analysis confirms the uniform distribution of C and O in the CA membrane, with N detected in the CA-CS membrane, validating successful chitosan incorporation. The addition of chitosan enhances the membrane's functional properties, introducing nitrogen-containing groups for improved mechanical strength. Mapping of the surface was done to observe the distribution of elements on the surface. In the CA membrane, it was observed that only carbon and oxygen were homogeneously dispersed. However, nitrogen was additionally found in the CA-CS membrane as elemental mapping. Similar has been observed by [358]

The static water contact angle of CA and composite film was recorded on the left and right sides of the sessile drop, as shown in **Fig. 4.3 (a) & (b)**, and the mean value is calculated. It can be observed that contact angles increased with the addition of CS in a hydrophobic CA matrix, and the blend films with Chitosan, i.e., CA-CS, have a water contact angle of 60.34° , indicating hydrophilicity in the composite. This is primarily due to the incorporation of CS in the CA matrix. The abundance of hydrophilic functional groups, including amino ($-\text{NH}_2$) and hydroxyl (OH) groups, increases membrane affinity for water molecules [359]. In contrast, the CA membrane has relatively fewer polar functional groups, exhibiting a smoother surface as confirmed by an AFM study. The relatively higher contact angle of 75.45° was observed. The reduction in contact angle in the composite membrane suggests an improved proton conductivity and anti-fouling behaviour, which are essential for efficient ion transport in bioelectrochemical systems like microbial fuel cells (MFCs). The significant decrement in the composite film helps to improve the interaction between the water and the membrane surface and enhance the efficiency of the MFC. Nevertheless, greater hydrophilicity and a resulting decrease in the water contact angle may also be caused by surface roughness. Despite being biodegradable, it is important to note that composite films have enough durability in water to

be utilised for MFC applications for longer periods as two-compartment separators and for heavy metal removal studies from wastewater. The chemical makeup and hierarchical micro/nanostructures of membranes are two crucial elements in preventing membrane fouling [360]. The root-mean-square roughness (R_q) was obtained from the AFM image (**Figure 4.3(c) & (d)**) of the membrane to determine roughness. Atomic force microscopy (AFM) revealed that the pure CA membrane had a root mean square (R_q) surface roughness of 19.82 nm, whereas the CA-CS composite membrane had an R_q value of 49.29 nm, which is much greater. The addition of chitosan (CS) to the cellulose acetate (CA) matrix is responsible for this noticeable rise in surface roughness. Through physical entanglement and hydrogen bonding, chitosan's unique molecular structure, which includes amino and hydroxyl functional groups, interacts with CA to create a more varied and textured surface morphology [361]. Additionally, surface imperfections are a result of the crosslinking process, which is frequently used with agents like glutaraldehyde and adds structural complexity and network creation. The composite membrane's enhanced surface roughness is important because it can increase the surface area accessible for interaction with ions and water molecules, boosting the membrane's hydrophilicity and proton conductivity [362]. The observed decrease in the water contact angle for the CA-CS membrane in comparison to the CA supports this. Furthermore, in microbial fuel cell (MFC) applications, the rougher surface might also encourage improved bacterial adherence and biofilm formation, which could improve electron transmission at the biofilm-anode interface. Therefore, the CA-CS membrane's higher R_q value suggests a fundamentally improved surface topology, which is essential for enhancing membrane performance in bioelectrochemical applications such as energy recovery and wastewater treatment. This topographical enhancement promotes a more robust electroactive biofilm formation, crucial for optimizing electron flux to the anode. Electron flux is the rate of electron transport per unit electrode area, which is directly proportional to the current density of the system [25]. Moreover, the heterogeneous nature of the copolymer matrix can fine-tune ion-selective

transport properties, reduce oxygen diffusion and increase proton conductivity. These improvements collectively optimize the membrane's ion exchange capacity and its role in biofilm development, ultimately augmenting the power output and operational stability of MFCs.

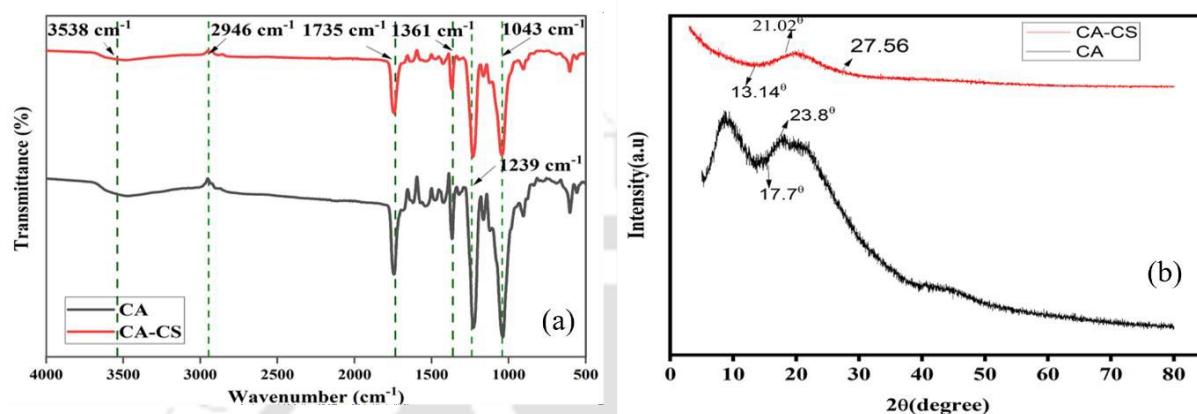


Figure 4.1. (a)FTIR and (b) XRD analysis of CA and composite membrane

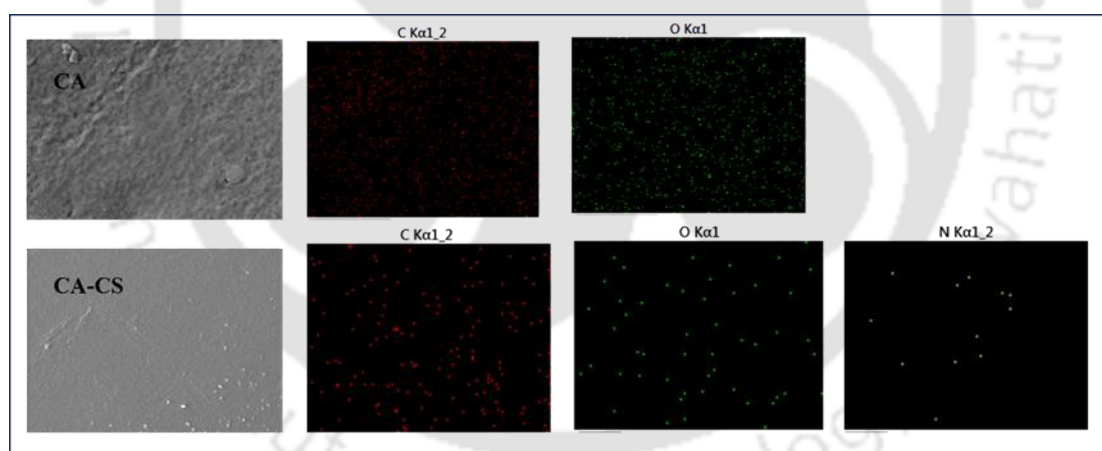


Figure 4.2. EDX analysis of fabricated membranes

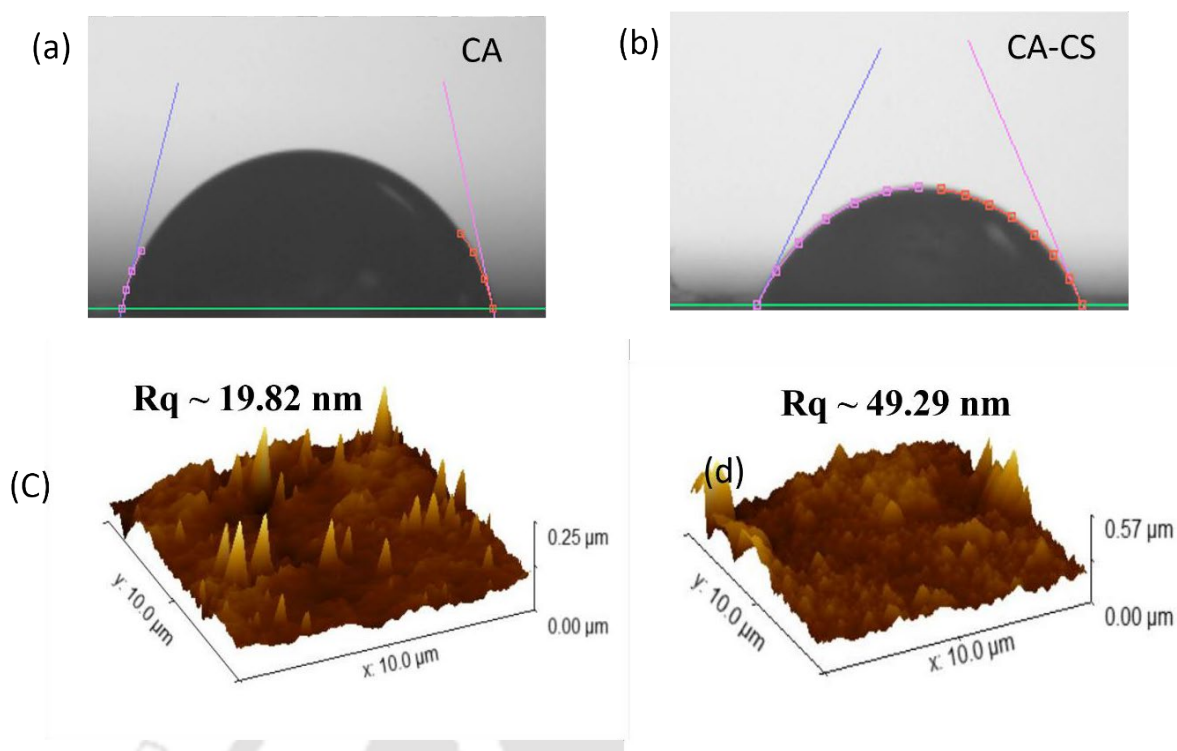


Figure 4.3. contact angle of (a) pure CA, (b) CA-CS film, (c) AFM analysis of (c) CA, (d) CA-CS composite film

4.2.2. Thermophysical properties of composite membrane

The DSC analysis of the composite film, as shown in **Figure 4.4 (a)**, displayed a distinct thermal behavior compared to the pure CA film. This variation can be attributed to the incorporation of chitosan, where strong hydrogen bonding, along with electrostatic and van der Waals interactions between the two polymers, altered the thermal transitions of the membrane [363], [364]. Similar has been reported in [365] [41]. The TGA/DTGA curves of the prepared CA-CS composite films are shown in **Figure 4.4(b)**. All of the membranes showed an initial weight loss of about 1.02% below 100 °C, which was brought on by the membranes' solvent and water evaporating, which is thought to be the first stage of degradation [367]. In the second step, the onset temperature (T_{onset}) showed a 50 wt% reduction, starting from 260 to 329 °C. The breakdown of the polymer backbone and the deacetylation of CA were the causes [368]. Since there was no change in mass, the third step, which involved the offset temperature (T_{offset}), revealed that the degraded products had carbonized to ash. The offset was set between 300 and

400 °C. After calculating the degradation time of the pure CA and composite film, we discovered that the T_{50} value of the Ca-Cs-based composite membrane was higher than that of the pure CA-based membrane. More precisely, a temperature of about 4°C was observed.

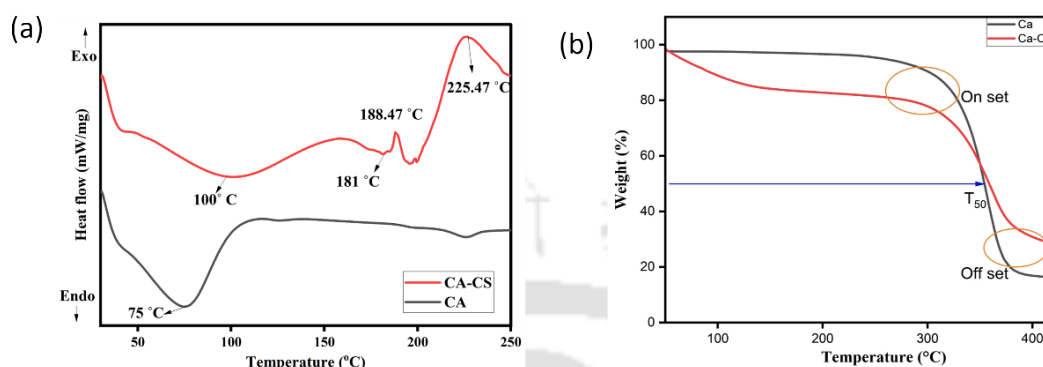


Figure 4.4.(a) DSC of fabricated film (b) TGA analysis of composite film

4.2.3. Mechanical properties of the composite membrane

Figure 4.5(a) & (b). represents the strain–stress curves of CA and CA-CS. The fracture stress and strain of the composite CA-CS film are 32.47 ± 1.30 MPa and 161.47 ± 8.07 %, unlike the neat CA film, which is 19.08 ± 0.80 MPa and 150.24 ± 7.5 %, respectively. A similar trend has been observed in Amany. A et al. (2021) [369] [370] [46]. The addition of glutaraldehyde as a crosslinker to the composite film increased the tensile strength approximately 1.70 times that of CA, and the corresponding elongation at break was 1.08 times that of the neat CA film. Adding a cross-linking agent to a polymeric film enhances the mechanical stability of the membrane by creating a network of bonds between polymer chains [372]. A similar effect has been observed. Cross-linking forms covalent bonds between polymer chains, reducing the flexibility of individual chains and making the material more rigid and resistant to deformation. The interconnected network allows the material to withstand greater stress without breaking, increasing its tensile strength. Also, the addition of chitosan in the CA matrix has also impacted tensile stress overpassing the [373] CA film [374]. This clearly indicates that the constituents

of composite films are either partly miscible or immiscible and exhibit some degree of interfacial adhesion. The intermolecular structure was comparatively stable, the hydrogen bonding at the interface was greater, and the CA's intermolecular forces were lessened when chitosan was added. Consequently, the composite film attained effective ductility and structural softening, which resulted in the improved mechanical characteristics that were observed.

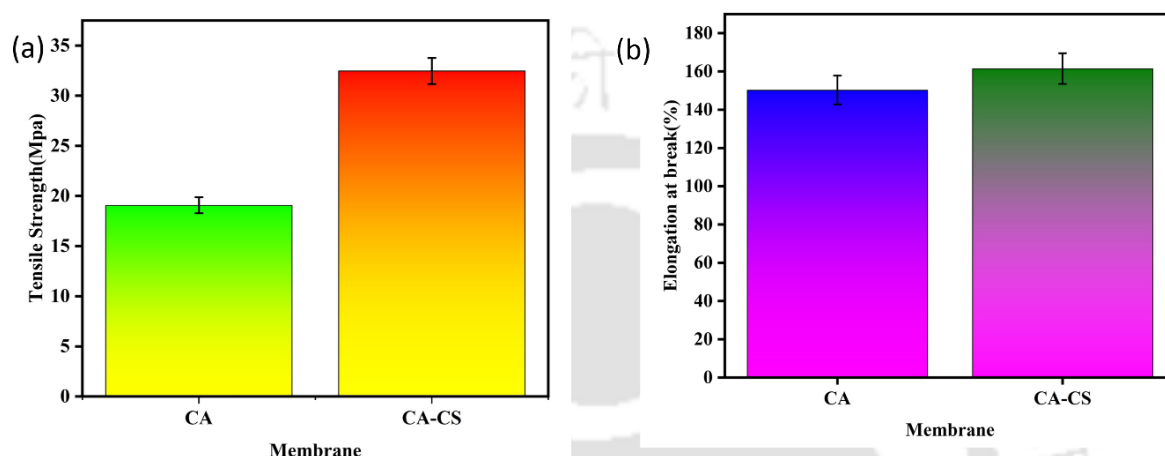


Figure 4. 5. (a) Tensile strength of fabricated film (b) Elongation at break of composite film

4.2.4. Antimicrobial Activity on Composite Film

A key obstacle obstructing the widespread deployment of microbial fuel cells (MFCs) is biofouling. Anode-side membranes are susceptible to biofouling, a surface phenomenon characterized by the accumulation of unwanted biofilm brought on by the growth of anodic bacterial populations over prolonged operation[375]. Because biofouling prevents proton transport across the membrane, it reduces the power output of microbial fuel cells. The anti-adhesive method, which prevents bacteria from adhering to the membrane surface, and the anti-microbial method, which actively destroys bacterial cells on the membrane, are the two primary approaches that can be used to address this issue. The changed membrane, which is the one with the fewest cells on its surface, as seen in the FESEM images, indicates that the bacterial cells are unable to adhere. This indicates that the anti-adhesion property is good. The rod-

shaped morphology of *E. coli* is highly prevalent in wastewater, especially from hospitals, residential areas, and industrial sewage. is depicted in **Figure. 4.6 (a) & (b)**. Furthermore, the originally rod-shaped cells have been ruptured. Consequently, the morphology of the damaged cells is evident, as shown in **Figure. 4.6 (c) & (d)**, clearly indicating that the membrane possesses high antimicrobial properties. The rupturing of the cells in the composite film is due to the presence of the amino group, which came from chitosan [376]. The glucosamine framework of the chitosan membrane has a significant concentration of amino groups. Thus, electrostatic interactions transpire between the cationic $-NH_2$ groups of chitosan and the anionic surface proteins and lipopolysaccharides of the bacterium. This interaction modifies the permeability of the microbial cell membrane, resulting in the release of intracellular constituents, hence causing cell rupture and eventual cell death. This result corresponds with the prior research conducted by Ref [377]. Following a 72-hour incubation period, the detrimental effect on the microbial cells is evident in the case of the CA membrane, as seen in **Figure. 4.6 (e)**. Upon interaction with the membrane surface, the bacterial cells experience a morphological alteration. The composite membrane demonstrated superior antibacterial characteristics compared to the CA membrane composite, attributable to the copolymerisation process. The amalgamation of chitosan and cellulose acetate enhances the membrane's hydrophilicity.

A more hydrophilic surface reduces bacterial adhesion, which is a key factor in biofilm and biofouling development. Also, it is demonstrated by the improved mechanical properties with high tensile strength and flexibility of the composite film in UTM analysis and controlled swelling of the composite film, as observed previously, which helps maintain membrane integrity under operation in microbial fuel cells for wastewater treatment.

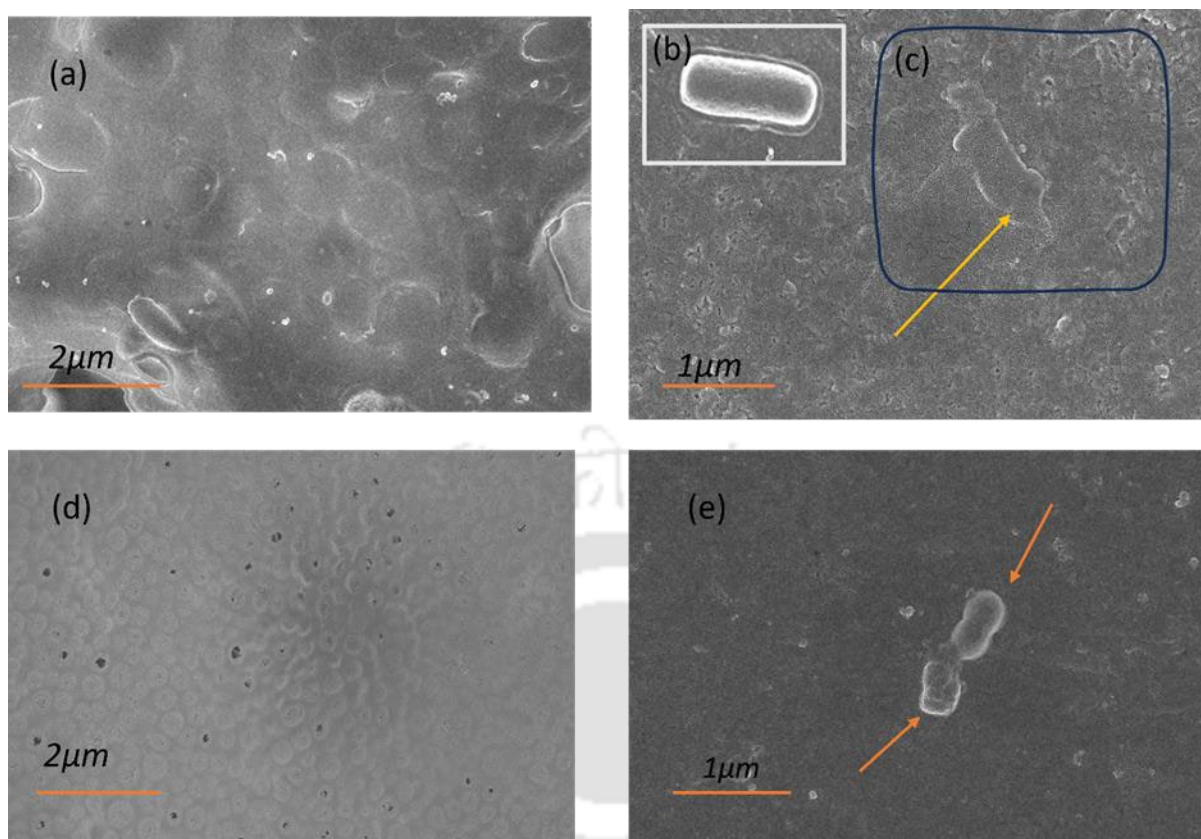


Figure.4.6. (a) Surface morphology of composite film prior to antibacterial evaluation, (b) inset image illustrating the actual rod shape morphology of *E. coli*, (c) detrimental effect on the bacterial cell in contact with the synthesised composite film, (d) surface morphology of CA membrane before antibacterial evaluation, (e) CA membrane exhibiting disrupted *E. coli* bacteria cells on its surface

4.2.5. Effect of composite membrane on COD and Chromium remediation

Hydrophilia for high ion transport, low resistance, and neutrality to prevent pH shift and ion selectivity, mechanical stability to withstand anti-biofouling and deformation, and qualities to guarantee steady power generation over an extended period are all necessary for the perfect separator [45]. The high cost of the membrane, its biofouling, and internal resistance during operation are the three factors that must be considered in order to make the membrane-using process feasible. Cellulose acetate is a non-toxic, biodegradable, and inexpensive polymer [378]. It is an inherently hydrophobic polymer, and a chitosan hydrophilic polymer, being blended, which makes it favourable for wastewater treatment. The fabrication of pure chitosan

membranes has been restricted because of their poor mechanical and chemical durability, particularly in an aqueous environment, despite extensive study on the creation of chitosan membranes for adsorptive separation [46], [47], [381]. Chitosan has often been applied to supports like cellulose membranes or polyether sulfone to enhance their mechanical qualities. Chitosan's uneven and insufficient covering on support membranes was inferior to composite materials because of its ease of separation. One efficient way to get around the drawbacks of pure chitosan is to blend it with other polymers [382], [383]. In order to remove dye, Daraei et al. created thin-film composite membranes employing nano clay and chitosan on polyvinylidene fluoride microfiltration substrate [332]. Separation of chromium and copper ions was conducted by Boricha and Murthy using N, O-carboxymethyl chitosan/cellulose acetate blend membranes [384]. Chitosan/polyacrylonitrile composite ultrafiltration membranes were prepared by Musale and Kumar and were used for heavy metal and microorganism separation from aqueous solutions [385]. The % COD removal for CA-CS-based BEC was also studied in 30 days of operation, as shown in **Figure 4.7 (a)**. Therefore, the bioelectrochemical MFC device can be used for organic matter removal along with energy generation. In this study, we investigated the heavy metal as potassium dichromate, removal efficiency on double-chambered MFC performance for 30 days. We have used both of our two membranes, named CA and the CA-CS composite film, on our MFC to examine the removal efficiency. Chromium concentration was determined using Atomic Absorption Spectroscopy (AAS), a widely accepted and reliable method for heavy metal quantification in aqueous systems. Similar approaches have been reported in chromium removal studies employing polymer-based and adsorbent systems. Similar approaches have been reported in chromium removal studies [26], [27], [28], [29], [30], [31]. It was observed that using CA-based BEC, potassium dichromate removal efficiency was approximately 83% while using the composite film-based BEC, the efficiency increased to 90%, as shown in **Table 4.1** and **Figure 4.7 (b)**.

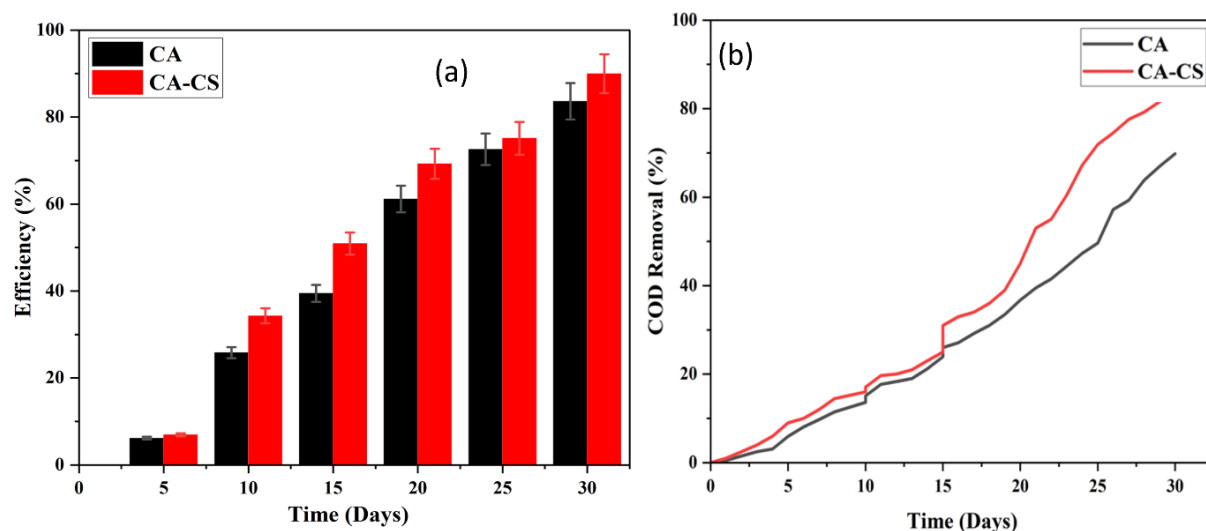


Figure 4.7. (a) Removal of Chromium, (b) COD removal of fabricated membranes based on MFC

Table 4.1. Summarises the different types of wastewaters used in the variable operation mode of the MFC system and the nutrient removal at certain conditions.

Wastewater type	Type of system/operation	Anodic volume	Cation Exchange Membrane	COD removal	Reference
Synthetic wastewater	Feed-batch mode MFC two stages	NA	Nafion -117	70-90%	[386]
Primary effluent of municipal wastewater	MFC system- Modularized, Continuous mode	200L	CEM, Ultrex CMI7000	>75%	[387]
Dairy industrial wastewater	MFC- double chambered continuous mode.	2L	Mediator less	90.46%	[204]
Untreated human urine	MFC-3-stage system continuous operating	6.25mL	CMI-7000, Membrane	20%	[388]
Domestic wastewater	MFC with biofilm algal growth. Continuous mode	500mL	NA	81.9%	[286]
Effluent drains of the vegetable oil industry	DCMFC- batch mode	2L	CMI-7000	60-90%	[389]
Digestate coming from	Seawater biterns for struvite crystallization. Batch mode, single chamber, air-cathode	28 mL	Nylon	44.7 ±1.6%	[390]

an anaerobic digester	MFC					
Synthetic domestic wastewater	photoautotrophic MFC of the H type, constant mode.	400mL	Nafion-117	93.2%	[391]	
Real municipal wastewater	Double-chambered Fed-batch mode	1L	CA-CS	83.4±0.1%	This study	

4.2.6. Electrochemical performance of the composite membrane-based MFC

Under the fed-batch mode of operation, utilizing a composite film of CA-CS and CA membranes, it took approximately two weeks to achieve stable conditions in the investigated MFCs. A consistent rise in voltage was observed with an external load of 1 k Ω . No substantial delay in voltage production was found at start-up, showing effective microbial cell-to-anode adhesion. Once the MFC achieved a consistent cell potential under specific experimental parameters, calculations were conducted to assess sustainable power generation. This assessment involved determining the relative variation in the anodic potential. To further understand the electron discharge characteristics of the biocatalyst, cyclic voltammetry (CV) was employed. This assessment was carried out using an Electrochemical analyzer (CHIE60 series). Using the anode and cathode as working and counter electrodes against an Ag/AgCl (sat KCl) reference electrode in the electrolyte, all electrochemical tests were carried out in situ. CV was carried out by applying a potential ramp to the working electrode over the +1.5 to -1 V range at a scan rate of 10 mV/s, as shown in **Figure 4.8 (a) & (b)**. Understanding the metabolic alterations and the electron carriers implicated in their transference is aided by the in situ assessment of the release of electrons using cyclic voltammetry (Vs Ag/AgCl (sat KCl)) with time. Without the use of any kind of biocatalyst,

electrochemical analysis demonstrated the significant variance in the electron discharge characteristics. The composite film CA-CS-based MFC showed peaks at -0.75V and +0.75V with a mixed culture of bacteria, while the CA-based MFC did not show a comparable pattern. The redox peaks observed in the CA-CS-based MFC (Fig. 4.8b) are attributed to extracellular electron transfer (EET) processes associated with electroactive microorganisms. These peaks arise from redox-active components such as membrane-bound cytochromes or soluble electron shuttles present within the biofilm, which facilitate electron transfer from microbial metabolism to the anode. The absence of similar peaks in the CA-based MFC suggests comparatively weaker biofilm–electrode interactions and reduced electrochemical activity. Energy losses occur as a result of the numerous challenges that electrons created by substrate degradation must overcome on their journey from the biocatalyst towards the anode, subsequently to the cathode. One could categorize these losses as activation losses. There is a significant similarity between biological and bio-electrochemical processes in that both require the responding species or biocatalyst to overcome an activation barrier [392]. These losses result in a cell voltage (V) that is inferior to its optimal potential. The voltage declines due to activation losses may be quantitatively expressed using a semi-empirical Tafel equation [393]. The electron losses that take place when they move from the biocatalyst to the anode and then to the cathode are explained by the Tafel diagram. Tafel plots offer a visual representation of a fuel cell's activation losses [394]. For each MFC operation, a Tafel plot for CA and CA-CS, as seen in **Figure 4.8 (c) & (d)**, was created in order to determine its kinetic characteristics, including oxidative slope. According to the Tafel equation, the exchange current densities (i_0) were computed at MFC's maximum performance since the Y-axis intercept is the logarithm of the densities ($\ln i_0$) [395]. After augmentation, the CA-CS-based MFC outperformed the CA-based MFC in terms of exchange current density, displaying 1.2 mA/m². Since the interchange between reactant and product states at equilibrium is represented by i_0 . With a lower forward reaction activation energy barrier, a greater value of i_0 indicates a faster rate of reaction [393]. Table 2 displays that

the Tafel slope for the composite CA-CS membrane-based MFC was less than that of CA. Higher electron transfer efficiency and bio-electrocatalytic activity are indicated by a lower Tafel slope.

The proton exchange membrane (PEM) is essential in the design of microbial fuel cells (MFCs). It performs the dual role of physically partitioning the anolyte and catholyte chambers while selectively permitting the migration of protons (H^+) towards the cathode. This proton transport is crucial for maintaining electroneutrality and completing the electrical circuit by compensating for the electrons traversing the external circuit. The use of actual wastewater as anolyte may markedly impact the membrane's characteristics, namely by modifying the ohmic resistance, hence influencing the overall electrochemical efficacy of the system. To evaluate the internal resistance, electrochemical impedance spectroscopy (EIS) was employed, linked to various membrane topologies. The EIS data were examined using the Randles equivalent circuit model, as seen in **Figure 4.9 (c)**. R_1 , R_2 , C_2 , and W_2 denote ohmic resistance, charge transfer resistance, double-layer capacitance, and Warburg impedance, respectively, each signifying elements of the internal resistance in the MFC system. The increased conductivity of hospital wastewater (HWW) facilitates ion mobility in the electrolyte, hence enhancing the overall electrochemical performance of the MFC. The internal resistance, namely the ion transport resistance, for both CA-based and CA-CS-based MFCs was assessed by EIS analysis, as seen in Figures 4.9(a) and 4.9(b). Electrochemical impedance spectroscopy was performed to evaluate the charge transfer characteristics of the microbial fuel cell. The impedance data were represented in the form of a Nyquist plot and analysed using the modified Randles circuit consisting of solution resistance (R_s), charge transfer resistance (R_{ct}), and constant phase element (CPE). In the Nyquist plot the semicircular region observed in the high to mid frequency range corresponds to the charge transfer process at the biofilm -anode interface. The diameter of the semicircle represents the charge transfer resistance (R_{ct}). From the fitted impedance data R_{ct} value of the composite film CA-CS exhibited a reduced charge transfer

resistance of 3.8Ω (as shown in **Table 4.2**) in comparison to the CA membrane, indicating efficient electron transfer kinetics and reduced interfacial resistance. The exchange current density value obtained is lower than the theoretical value; this is due to the complex bioelectrochemical nature of the anode reaction. In contrast, the ideal electrochemical systems electron transfer in MFCs is mediated by electroactive biofilms, extracellular polymeric substances, and metabolic pathways of microorganisms. Additionally, factors such as mass transport limitation, biofilm heterogeneity and internal resistance contribute to reduced effective current density. Similar results have been reported by Santoro et al. (2017), where electron transfer efficiency was strongly influenced by interfacial resistance and biofilm conductivity [32]. Similarly, Ha et al. (2010) demonstrated that charge transfer resistance is directly associated with biofilm development and plays a key role in MFC performance [33]. The enhancement is attributed to the synergistic interaction between copolymerization of celluloseacetate and chitosan, combined with the crosslinking effect of glutaraldehyde (GA), which improves membrane structural stability, regulates swelling, enhances proton transport, and optimizes electrochemical performance [396]. As illustrated in **Figure 4.9 (d)**, the coulombic efficiency of the composite film CA-CS-MFC was 92.18%. This is higher because the composite film, used as both a separator and a proton exchange membrane, is hydrophobic. Additionally, the honeycomb-like configuration of MF has resulted in improved laminar fluid flow of the anode compartment, which enhances the mass transfer process between ions and substrate in wastewater for efficient secretion of extracellular polymeric substance (EPS) matrix on the anode surface of the electrode, leading to stable biofilm development. on the electrode surface. Also, because there is less diffusion of oxygen from the cathode to the anode and substrate from the anode to the cathode. Similar has been reported by [397][244][398].

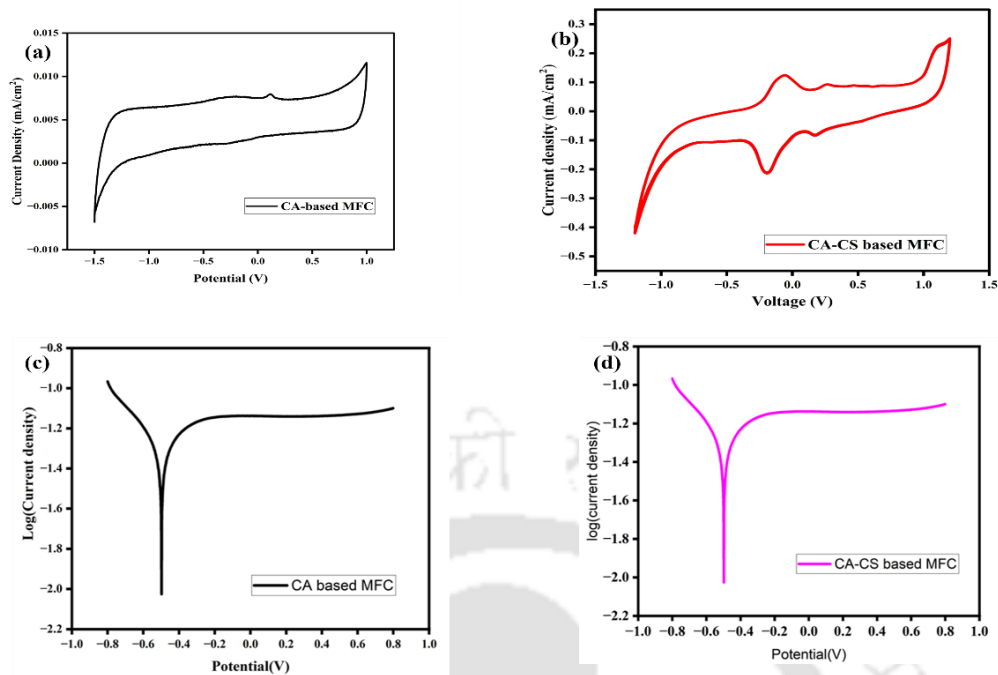


Figure 4.8. (a) cyclic voltammetry of CA, (b) CA-CS composite membrane-based MFC, (c) Tafel plot of CA-based (d) Composite membrane-based MFC

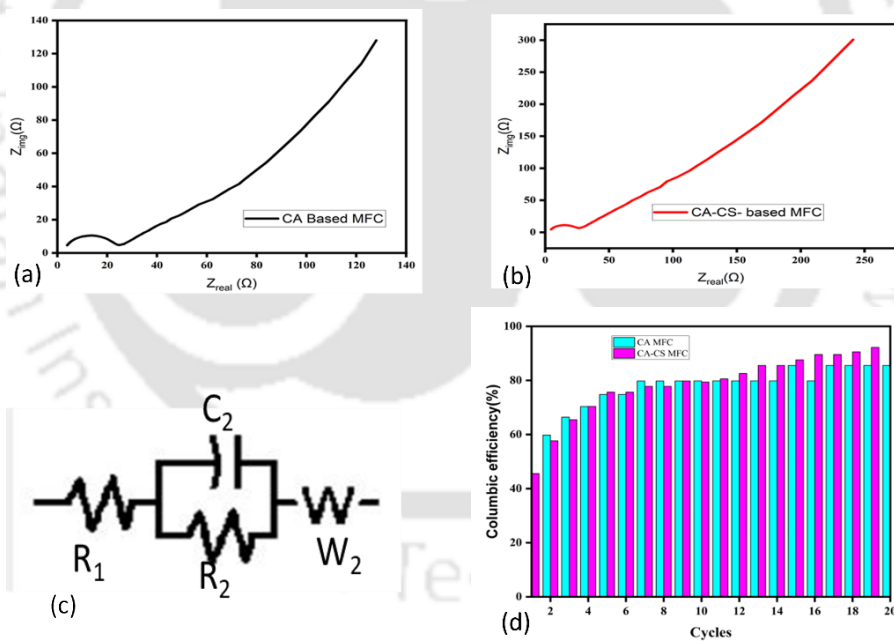


Figure 4.9. (a) Nyquist plot of CA-based, (b) CA-CS-based MFC, (c)Equivalent circuit of the MFC, (d) coulombic efficiency of CA and composite membrane-based MFC

Table 4.2. Electrochemical performance of the composite membrane and the CA membrane-based MFC

Membrane	CA-based MFC	CACS-based MFC
Maximum open-circuit potential (mV)	623±0.5	756±0.6
Ohmic resistance (R_1) Ω	29	27
Charge transfer resistance(R_2) Ω	4.96	3.8
Exchange current density (i_0) mA/m ²	0.96	1.2
Tafel slope (β_0) mV/dec	0.46	0.17

4.2.7. Biofilm analysis

A new, bacterial-free medium was used instead of the culture once the microcell's ability to function as an MFC was confirmed. Given that the operating circumstances used permitted the growth of both free-living cells suspended in the anolyte's bulk and a microbial biofilm adhered to the anode, it was vital to determine each component's specific contribution. Rod-shaped bacteria were discovered when the biofilm layer on the graphite felt electrode was closely examined (**Figure 4.10 (a)**). For enhancing the performance of Microbial Fuel Cells (MFCs) when fed real hospital wastewater, a mixed consortium is preferred over a pure culture. It is said to be preferred because it exhibits a "nutrient cycle ecosystem." Some species in this ecosystem are in charge of breaking down organic debris, while others try to reverse the negative effects of the contaminants in the wastewater. This dynamic interaction leads to enhanced performance compared to a system relying solely on a pure culture. The process of biofilm formation undergoes three steps, namely, adhesion on the electrode surface, maturation, and then detachment. A crucial factor in power generation is the conductivity of the biofilm

formed by the electrogenic process. The FESEM pictures of the graphite felt electrode before and after biofilm growth on the anode electrode, using hospital wastewater as the substrate, are displayed in **Figure 4.10 (b)**. The hair-like projections known as pili, which are seen to connect the bacterial cells, are essential for both transporting electrons from the microorganisms to the anode and forming a stable biofilm on the anode surface [399]. The low R_{ct} value in the EIS study indicates that the persistent biofilm that formed preferred low resistance to the electrochemical process at the anode surface.

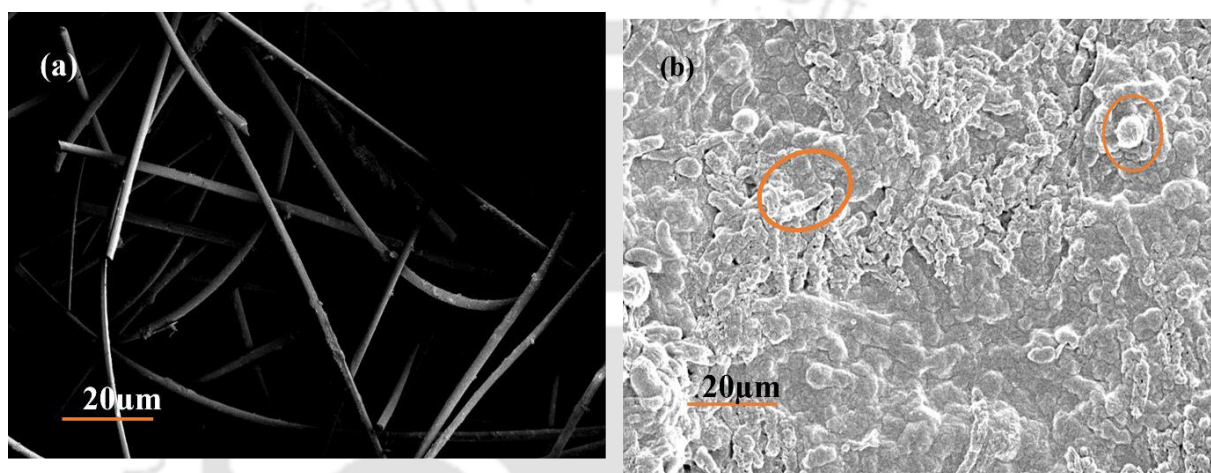


Figure 4.10. (a) Electrode surface without biofilm. (b) The development of biofilm on the surface of the electrode

4.2.8. Cost Analysis

The economic feasibility of membrane technology is essential for its use in large-scale industrial operations. Polymeric membranes in these applications typically cost between \$50 and \$200 per square meter. Microbial Fuel Cells (MFCs) fulfil a dual function in energy generation and wastewater treatment, offering a sustainable approach to transforming waste into energy, hence reducing energy costs and waste management expenditures. Nonetheless, a major constraint on the economic feasibility of MFCs is the substantial capital expenditure, with around 65% ascribed to the Nafion 117 membrane. This significant cost is a substantial barrier to the widespread use of MFCs.

This project intends to create an economical, crosslinked bio-composite membrane and conduct a comprehensive analysis of its capital expenditure. The objective is to substantially lower the total expenses of MFC systems while maintaining efficient performance in actual wastewater treatment contexts. The cost assessment for the synthesised membrane considers the expenditures associated with chemicals, power, and labour during production, as detailed by Sarma and Mohanty (2023) [400]. Nafion 117 was acquired from the Indian market for ₹25,370 (~USD 300) per 900 cm², enabling a direct cost-performance comparison between the traditional and the newly created membrane. This cost-centric strategy highlights the potential of sustainable membrane alternatives to replace costly commercial choices and improve the scalability of MFC technology. The total production cost of the crosslinked membrane was determined by assessing expenses for raw materials, energy consumption, and labour costs, as shown in **Table 4.3**. Equipment, power specifications, operational duration, and energy tariffs together influence the overall cost of electricity use.

The equation used for calculation is

$$C_e = P * n * t$$

Equation 6

where C_e signifies the energy consumption cost, P represents the power consumption of the equipment (in kW), n denotes the number of operational hours, and t shows the electricity price. The synthesis process used 5 kWh of energy, whereas annealing required an additional 7.3 kWh, at a rate of ₹5.96 per kWh as illustrated in the **Table. 4.4**. The costs for workers were calculated based on a skilled worker wage of ₹954 (approximately \$ 11.12 USD) per day, as per the Ministry of Labour & Employment, India, with an additional 20% allocated for laboratory expenses. The total cost of the crosslinked membrane was ₹3,906.01/ft² (1 USD = 85.76 INR), which is 6.87 times less than Nafion 117 (₹26,831.84/ft²), hence offering a viable and economical alternative for MFC applications.

Table 4.3. Calculation of energy consumption based on power rating and operating time of equipment used in membrane fabrication

Process	Equipment	Power (KW)	Time (h)	Energy
Stirring	Magnetic stirrer	0.1	6	0.6
heating	Hot plate	1.0	3	3.0
Sonication	Ultrasound	0.2	2	0.4
Drying	oven	0.5	2	1.0
Total				5KWh

Table 4.4. Breakdown of costs for the manufacture of the composite membrane

Ingredient	Price/g USD	g/ft ²	Price/ft ² USD
Cellulose acetate	0.25	1.2	0.3
chitosan	0.012	0.6	0.0072
Glacial Acetic acid	0.05	5.25	0.26
Glutaraldehyde	0.50	6.31	3.16
Membrane casting (labour, electricity)			41.9
Total			45.62
PFASs commercial membrane			312.9

4.3. Conclusions

This work successfully created a cost-effective and environmentally acceptable biocomposite membrane using a combination of cellulose acetate (CA) and chitosan (CS), crosslinked with glutaraldehyde, for use in an MFC treating hospital effluent. The integration of chitosan into the CA matrix markedly improved the membrane's hydrophilicity, mechanical strength, proton conductivity, and anti-fouling characteristics. The CA-CS composite membrane exhibited enhanced electrochemical performance, characterised by increased coulombic efficiency of 92.18%, superior COD removal of $83.4 \pm 0.10\%$ and heavy metal removal. The composite CA-CS membrane-based MFC, supplied with actual wastewater, demonstrated a peak exchange current density of 1.2 mA/m^2 , due to the minimal charge transfer resistance of 3.8Ω , as verified by EIS analysis. The reduced resistance signifies accelerated electrochemical processes, improved catalytic activity, and more effective electron transport between the microbial biofilm and the electrode contact, as confirmed by SEM analysis of the biofilm formation on the electrode surface. Moreover, its bio-derived, biodegradable characteristics provide a viable substitute for costly and ecologically detrimental commercial PFAS-based membranes such as Nafion. Surface morphology indicates that CA-CS composite membranes exhibit antibacterial and antifouling properties, enhancing the long-term stability and performance of MFC systems while significantly contributing to green energy production and sustainable wastewater management, under global Sustainable Development Goals (SDGs 6, 7, and 12). Cyclic voltammetry reveals the presence of electroactive species and electron transfer processes within the microbial consortium. The observed redox peak suggests active microbial behaviour. Additionally, FESEM analysis reveals interconnected microbial structures resembling Pili to facilitate extracellular electron transfer. The cost study reveals 6.86 times decrease in manufacturing expenses relative to the traditional Nafion membrane option. The crosslinked composite membrane has significant eco-friendly characteristics due to its catalyst-free production and the use of water as a sustainable solvent, unlike the toxic NMP often used for

polymer dissolution in existing research. Moreover, the membrane needs no additional pretreatment or activation procedures, in contrast to conventional PFAS-based membranes that require rigorous chemical conditioning. These benefits substantially reduce environmental impact during both production and disposal, establishing the crosslinked composite membrane as a more ecological and economically viable option for practical use in microbial fuel cells (MFCs). Although the proposed membrane has promising performance under laboratory conditions, its practical applicability in large-scale systems remains unverified. Additional validation under actual operating situations is necessary. This phase is essential for progressing towards industrial implementation and regulatory endorsement. This techno-economic study is confined to laboratory-scale costs and direct material price, without consideration of large-scale production, durability, or waste management. Fluctuations in commercial membrane costs may also affect relative savings. Future pilot-scale and life cycle analyses are required for a more thorough evaluation.

Chapter-5

Next Generation per and poly-fluoroalkyl-free graphene oxide modified cellulose ether charge separator for antibiotic micropollutant removal and energy recovery in hospital wastewater-fed microbial fuel cell

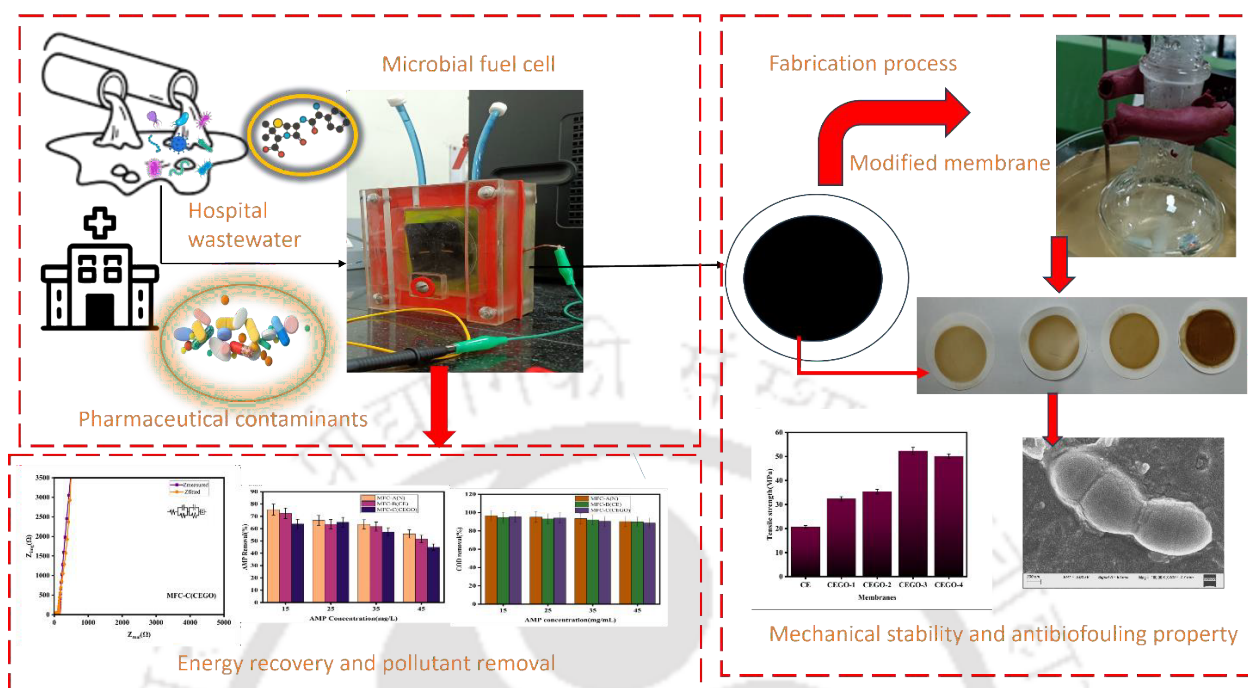
Motivation

The growing prevalence of antibiotic micropollutants within hospital wastewater represents a significant danger to both aquatic environments and public well-being, thereby necessitating the implementation of treatment technologies that are both efficient and environmentally sound. While conventional microbial fuelcells frequently utilise PFAS-based membranes, their electrochemical efficacy is counterbalanced by environmental and long-term toxicity issues. Consequently, there is a compelling need to develop next-generation charge separators that are free from per- and poly-fluoroalkyl substances, in accordance with the principles of green chemistry and the circular economy.

The work in this chapter is published as

Aparajita Roy, Sonu. Kumar, Kuhelika Das, et al., “ Next-Generation Per and Poly-Fluoroalkyl-Free Graphene Oxide Modified Cellulose Ether Charge Separator for Antibiotic Micropollutant Removal and Energy Recovery in Hospital Wastewater-Fed Microbial Fuel Cell,” *Journal of Polymer Science* (2026): 118, SN - 2642-4150 <https://doi.org/10.1002/pola.70044>

Graphical Abstract



Abstract

This chapter examines the design and use of a new charge separator for microbial fuel cells. It is made from graphene oxide-modified cellulose ether and is free of PFAS. The rising occurrence of pharmaceutical contaminants in aquatic systems, particularly antibiotics such as ampicillin, demands innovative treatment solutions capable of coupling pollutant removal with resource recovery. Conventional PFAS-based membranes like Nafion, commonly employed in microbial fuel cells (MFCs), pose environmental challenges due to their persistence and toxicity. This paper presents a graphene oxide-modified cellulose ether membrane with antifouling properties, designed as a PFAS-free alternative, and comprehensively assessed for its dual capacity to eliminate ampicillin while producing bioelectricity from hospital wastewater. Physicochemical analysis demonstrated that the addition of graphene oxide (GO) enhanced membrane hydrophilicity and mechanical stability, resulting in a 2.53-fold improvement in tensile strength relative to pure cellulose ether, while simultaneously decreasing substrate crossing. When used in a microbial fuel cell (MFC), the CEGO membrane promoted augmented microbial electroactivity and enabled more effective electron transfer, attaining a peak current density of 86.6 mA cm^{-2} . The enhanced electrochemical production, with a corresponding coulombic efficiency of 59.3%, was followed by a significant ampicillin degradation of 96.2%, highlighting the interaction between optimised proton transport and reinforced microbe electrode interactions. The membrane demonstrated operational stability in high-COD circumstances of hospital wastewater, signifying robust structural resilience and prolonged application. This study presents an innovative, sustainable, and ecologically friendly membrane platform that addresses the shortcomings of PFAS-based materials.

5.1. Introduction

The increasing worldwide issues of environmental contamination have always been a central subject of scientific research and politics. Although traditional pollutants like heavy metals and persistent organic pollutants have been rigorously monitored, a new category of chemicals, referred to as emerging pollutants (EPs) or contaminants of emerging concern, has attracted considerable attention in recent decades. EPs are characterised as manmade or naturally occurring substances that are not regularly monitored or governed by existing environmental legislation. They provide a potential or established harm to natural ecosystems and human health [401]. These compounds, including medications, personal care products (PCPs), endocrine-disrupting chemicals (EDCs), pesticides, and industrial additives, result from contemporary urban, industrial, and agricultural practices [402]. The prevalence of these pollutants arises from their ongoing release into the environment via various channels, such as the effluent from municipal wastewater treatment facilities, agricultural runoff, and industrial discharges [403]. Despite their frequent occurrence in aquatic systems at trace quantities (nanograms to micrograms per litre), their continuous release and intrinsic characteristics, including persistence and potential for bioaccumulation, elicit concerns over chronic exposure consequences [404]. Electromagnetic pulses (EMPs) have shown the capacity to elicit several detrimental effects on non-target animals, including endocrine disruption in aquatic species and the facilitation of antibiotic resistance [405]. The detection of these compounds in drinking water sources, soil, and even the food chain highlights the need for a comprehensive understanding of their fate and transport. The zero liquid discharge (ZLD) methodology guarantees the reduction or complete cessation of wastewater discharge into the environment (Tarrass et al., 2021). In light of the worldwide transition to a sustainable circular economy, the management of hospital wastewater is progressively focusing on zero liquid discharge (ZLD) treatment solutions [406]. Regulatory entities, including the U.S. Environmental Protection

Agency (EPA) and the European Union (EU), are enhancing protocols to oversee and alleviate biohazards, pharmaceutical residues, and PFAS pollution in wastewater, to protect environmental and human health [407], [408], [409]. Ampicillin is a broad-spectrum β -lactam antibiotic that is a semi-synthetic penicillin, obtaining its antimicrobial properties from the presence of a beta-lactam ring [410]. Ampicillin is extensively used for a range of infections, such as gonorrhoea, urinary tract infections, and prevalent ear, nose, and throat conditions. Nevertheless, like other antibiotics, it is inadequately metabolized in the human body and is mostly eliminated in its active form via urine and faeces. The environmental durability of this substance is becoming concerning, since it facilitates the proliferation of antibiotic-resistant microbes. Research demonstrates that around 35 to 40% of *E. coli* isolates exhibit resistance to ampicillin, but over 95% of *Klebsiella pneumoniae* isolates are inherently resistant. Despite the technical and financial challenges associated with the removal of ampicillin from pharmaceutical and hospital wastewater, proper treatment is crucial to minimise environmental discharge and mitigate the rise of antibiotic resistance. Recently, several strategies have been used to eliminate pharmaceutical chemicals from aqueous solutions, including flocculation, flotation, photocatalysis, membrane processes, adsorption, and improved oxidation methods [411]. Various adsorbents, including commercial activated carbon (CAC), have shown considerable effectiveness in removing diverse pollutants from liquid waste streams. Nevertheless, CAC incurs substantial costs in prolonged treatment procedures, and its regeneration often demonstrates complexity and resource intensity [412], [413], [414].

Microbial fuel cells (MFCs), a unique category of bio-electrochemical systems, offer a self-sustaining and environmentally sustainable method for wastewater treatment by allowing electroactive microorganisms to convert the chemical energy in organic or inorganic pollutants into electrical energy via synchronised bio-electrochemical reactions. This new technology

adheres to the 4Es Energy, Environment, Efficiency, and Economics, providing the combined advantage of successful pollution cleanup and less reliance on fossil fuels, so promoting overall sustainability [415], [416]. Although significant progress has been made in recent years on employing MFCs to treat diverse wastewaters and remove antibiotics, including chlortetracycline, roxithromycin, norfloxacin, and sulfonamides, as highlighted by Zhang et al., the field continues to evolve with growing interest and innovation [417]. Likewise, Yang et al. [418] indicated that low dosages of sulfamethoxazole improved MFC performance, but higher amounts had inhibitory effects. Their results indicated that current intensity was more pivotal in antibiotic elimination than anode potential. Similarly, Li et al. showed that a modest concentration of tetracycline (10 mg/L) may be effectively and swiftly destroyed in a microbial fuel cell (MFC), highlighting a synergistic relationship between microbial metabolism and electrochemical stimulation. Nonetheless, the overall efficiency of MFCs is sometimes constrained by the substantial aeration requirements of the cathode chamber, which may account for up to 50% of the total operating expenses [419]. An effective strategy for substantially lowering overall expenses is the creation of an economical membrane to substitute Nafion, which accounts for around 38% of the entire capital outlay [420]. While membrane-less systems save costs by excluding the PEM, they concurrently experience increased internal resistance, which constrains performance. Consequently, the integration of a membrane separator is crucial for the steady and effective functioning of dual-chamber MFCs [276]. The membrane enables proton transfer crucial for preserving electro-neutrality while concurrently minimizing oxygen and substrate crossover, hence improving and stabilizing the open-circuit voltage [421]. An effective separator must demonstrate significant hydrophilicity to enable fast ion transport with minimal resistance and be chemically inert to avoid pH variations or undesired ion selectivity. It should possess mechanical robustness for sustained operation and demonstrate resistance to biofouling to maintain a consistent power output over time [422].

Biomass, being one of the most abundant energy resources on Earth, offers significant renewability and widespread availability. Its versatility makes it a strong candidate for the advancement of low-energy, high-efficiency, and environmentally sustainable energy systems. Consequently, biomass is sometimes seen as a vital element or the cornerstone of the emerging global bio-economy [423]. Cellulose is the most abundant biopolymer worldwide, with several beneficial properties like widespread availability, excellent biocompatibility, inherent biodegradability, and diverse chemical reactivity [424]. Native cellulose is infusible and has limited solubility in most conventional solvents owing to its strong intra- and intermolecular hydrogen bonding network, which significantly limits its direct processing and broader use [425]. This issue may be effectively resolved by converting cellulose into soluble derivatives, such as cellulose esters or cellulose ethers (CEs). These chemically modified versions enhance solubility and provide other functional advantages, including increased water-retention capacity, antibacterial characteristics, and responsiveness to external stimuli, therefore greatly expanding the applications of cellulose in advanced materials. Commercial cellulose ethers are extensively used and have significant relevance in pharmaceutical applications, serving functions that range from fundamental to very intricate. They may serve as dissolution-controlled coatings for extended drug release or undertake more complex roles, such as improving the solubility and bioavailability of poorly soluble pharmaceuticals. This discourse emphasises the cellulose ethers now accessible on the market, alongside those previously manufactured, while also examining some significant cellulose-based ether esters used in medicinal formulations. In order to tune the properties, impermeable nanofiller distribution in a polymer matrix has been demonstrated to have enhanced barrier and mechanical properties. Recent improvements have investigated the integration of diverse nanomaterials such as zeolite, carbon nanotubes, graphene oxide, and titanium dioxide into reverse osmosis polymeric membranes to improve their overall performance [426]. Incorporating these

nanoscale additions has shown a considerable enhancement in water permeability, augmented resistance to biofouling and chlorine degradation, and increased mechanical strength of the membranes, thereby prolonging operational lifetime and efficiency [427]. Numerous recent studies have focused on improving the characteristics of cellulose acetate by the integration of graphene oxide (GO). The incorporation of GO has demonstrably enhanced essential performance characteristics, including mechanical strength and thermal stability, making the material more resilient and more appropriate for rigorous separation and fuel cell applications [428] [429] [430][340].

To our knowledge, the alteration of cellulose ether membranes with graphene oxide has not been investigated for microbial fuel cell (MFC) applications, especially for the concurrent elimination of emerging pharmaceutical contaminants like ampicillin from hospital effluent. This work included the manufacture of graphene oxide modified cellulose ether membranes at different ratios to produce a variety of CEGO composite membranes. The impact of various blend compositions on essential physicochemical properties, such as water uptake, substrate crossover analysis, anti-fouling attributes, mechanical properties, hydrophilicity, organic matter elimination, and ampicillin degradation, was methodically assessed to determine their viability as PFAS-free membrane alternatives. Despite the increasing interest in MFC-based treatment of waste streams, little research has investigated how customized proton exchange membrane (PEM) alterations directly affect the bioelectrochemical behavior of indigenous microbial consortia in such complicated real hospital wastewater.

To address this gap, the present work also investigates how the newly developed modified PEM enhances microbial activity and consequently improves energy recovery efficiency, offering new insight into membrane microbe interactions within hospital effluents. The integration of a hybrid membrane with microbial fuel cells (MFCs) presents an innovative method for sustainable pollutant degradation and enhances energy recovery from hospital wastewater.

5.2. Results and Discussion

5.2.1. Water uptake and surface wettability of the modified membrane

The water absorption and swelling after incorporating graphene oxide (GO) into the cellulose-ether (CE) matrix is mostly attributable to the hydrophilic oxygenated functional groups on GO sheets. The polar groups establish significant hydrogen-bonding interactions with water and the hydroxyl groups on cellulose, so enhancing the composite's affinity for water and facilitating increased water sorption and matrix expansion. This process aligns with many studies indicating improved hydration and proton-transport characteristics after the incorporation of GO into polymeric membranes [431]. Water adsorption capacity was evaluated by a standard gravimetric method to assess membrane hydrophilicity and its influence on ion transport. Membrane samples were dried to constant weight, immersed in deionised water for 24 h, and reweighed after removing excess surface moisture. The percentage of water adsorption was calculated using the equation given [34]. The water absorption capacity and swelling of the CEGO-3 membrane were measured at $58.2 \pm 2.9\%$ and $75.75 \pm 3.7\%$, as shown in **Figure 5.1. (a) & (b)**. At low-to-moderate graphene oxide (GO) loadings, exfoliated GO sheets enhance the available surface area and generate supplementary hydrophilic sites and nanochannels that promote water absorption; this phenomenon accounts for the modest increases from $42.3 \pm 2.1\%$ (pristine cellulose ether) to higher values in GO-modified films. The correlation between GO content and hydration is not precisely linear. Numerous experimental studies have recorded the conflicting equilibrium between enhanced hydrophilicity and aggregation-induced densification when the loading of graphene oxide is beyond an ideal threshold [432], [433]. Consequently, slight augmentations in swelling from $72 \pm 3.6\%$ for pristine Cellulose ether to higher values are anticipated when GO is well disseminated and provides hydrophilic sites. The rise in graphene oxide (GO) content was carefully monitored and quantified to achieve the required hydration qualities via enhanced water absorption. These materials together provide a composite film distinguished by improved

hydrophilicity and structural stability, making it extremely suitable for extended use in microbial fuel cell (MFC) systems. Contact angle (CA) measurements provide critical information on the surface wettability and hydrophilicity of membrane materials, which profoundly influence proton transport and microbial adhesion in microbial fuel cells (MFCs). The pristine CE membrane exhibited a contact angle of $69.2 \pm 3.4^\circ$, indicating moderate hydrophilicity due to the presence of hydroxyl and ether groups. The addition of GO resulted in a gradual reduction of the contact angle, indicating enhanced surface hydrophilicity. Membranes with 0.2%, 0.4%, 0.8%, and 1.6% GO loading exhibited contact angles of $67.2 \pm 3.3^\circ$, $65.4 \pm 3.2^\circ$, $63.4 \pm 3.1^\circ$, and $61.2 \pm 3^\circ$, respectively, as seen in Figure 5.1. (c). The reduction of up to 0.8% GO highlights the importance of oxygen-containing functional groups on GO, which augment water affinity via hydrogen bonding interactions. As the concentration of graphene oxide (GO) increased, the corresponding rise in water absorption was carefully monitored and adjusted to provide the necessary hydration characteristics. The hydrophilic functional groups on graphene oxide enhance the membrane's affinity for water, while the cellulose ether matrix offers more sites for water interaction. The incorporation of GO enhanced the physicochemical characteristics and mechanical integrity of the membrane [434].

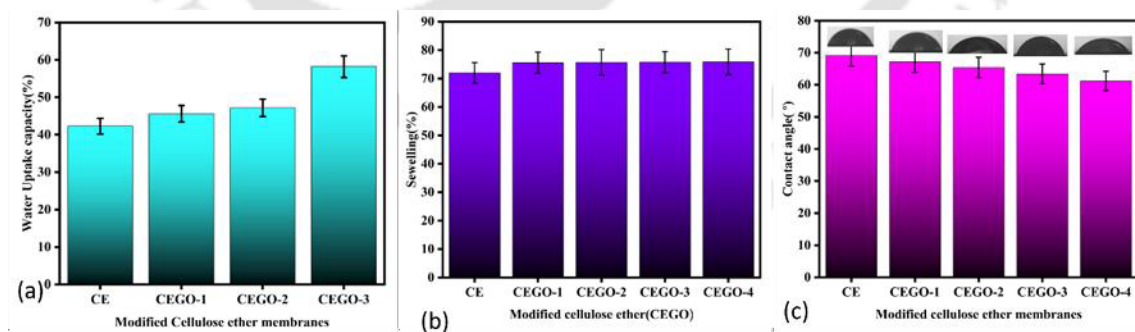


Figure 5.1. physiochemical property of the modified membrane (a) water uptake capacity, (b) swelling and (c) contact angle analysis on different concentrations of GO content

5.2.2. Physicochemical properties of Modified Membrane

X-ray diffraction (XRD) analysis was performed to investigate the structural modifications and crystalline characteristics of the graphene oxide (GO)- modified cellulose ether (CEGO) membrane. The diffraction patterns revealed distinct differences between pristine CE and GO-incorporated CE membranes, indicating the successful structural integration of GO within the polymer matrix. The characteristic diffraction pattern of the CE appeared at 9.35° [435]. This peak signifies the interlayer spacing (d-spacing) of GO, typically around 0.8–0.9 nm, attributed to the presence of oxygen-containing functional groups such as hydroxyl, carboxyl, and epoxide moieties that increase the interplanar distance [436]. The maximum intensity diffraction peak exists around $2\theta = 20.5^\circ$ in the GO-modified membrane, which indicates its semi-crystalline structure; it is comprised of both amorphous and crystalline regions as shown in **Figure 5.2 (a)**. The antifouling membrane exhibits a small shift due to incorporating the two surfaces of CE and GO, and the formation of the nanocomposite makes a distortion in the crystal lattice of the two surfaces, so the small shift of the pattern appeared in the CEGO membrane. A similar broad peak was observed in the XRD pattern in other studies [437], [438]. FTIR analysis is an essential method for qualitative material characterisation, facilitating the identification of organic and inorganic functional groups. The functional groups of GO-modified cellulose ether (CEGO) and commercial cellulose ether membranes were analysed using FTIR spectroscopy (**Figure.5.2(b)**). The CE membrane had a wide absorption band at 3481.85 cm^{-1} , indicative of the O–H stretching vibration of hydroxyl groups. The absence of this signal in the spectra of the CEGO membranes indicates effective alteration and interaction between GO and the CE matrix [439]. The distinctive peaks of C=O (1742.52 cm^{-1}), C-CH₃ (1807 cm^{-1}), CH₂ (1369.53 cm^{-1}), C-O (1225.67 cm^{-1}), C-O-C (ether linkage) (1043.74 cm^{-1}), and CH (904.44 cm^{-1}) were seen at approximately identical positions in both instances [224] [440]. Moreover, the results were validated by Raman spectrum analysis, as seen in

Figure 5.2(C). Raman spectroscopy enables the identification of organic and inorganic functional groups in the synthesised material. The GO-modified cellulose ether (CEGO) exhibited a significant Raman peak at 872.95 cm^{-1} , confirming the successful incorporation of GO into the cellulose ether matrix. Furthermore, the characteristic CO stretching of the carboxyl–carbonyl group and the stable C=C bonding were seen before to and after the oxidation of graphite, as shown by the two different peaks at 1721 cm^{-1} and 1610 cm^{-1} , respectively [441] [442] [443]. The XPS spectra of the CEGO membrane confirmed the successful modification of cellulose ether with graphene oxide, shown by the appearance of discrete carbon and oxygen peaks. The survey spectra (**Figure 5.3**) exhibited two significant peaks at C 1s ($\sim 284.6\text{ eV}$) and O 1s ($\sim 532\text{ eV}$), thus validating the presence of oxygen-containing functional groups introduced by graphene oxide (GO) as in **Table 5.1**. The O 1s spectra revealed contributions from C=O ($\sim 531.2\text{ eV}$) and C–O ($\sim 532.7\text{ eV}$) species, indicating the existence of several oxygenated functionalities that enhance hydrophilicity and interfacial compatibility [444] [445]. The findings validate the formation of strong interfacial interactions between cellulose ether chains and graphene oxide through hydrogen bonding and possible esterification, thereby improving electron transport pathways and surface wettability, which are essential for superior electrochemical performance in microbial fuel cell applications [446].

Table 5.1. XPS peak of the deconvolution results showing binding energy, chemical states and functional groups in both cellulose ether and GO- modified Cellulose ether

Spectrum	Binding energy	Assignment	Functional groups
C1s	284.6	C-C/ C-H	Polymer backbone
C1s	~ 286	C-O	Ether
C1s	~ 288.5	O-C=O	Carbonyl/ Ester
O1s	~ 530.5	C=O	Carbonyl
O1s	~ 532	C-O	Hydroxyl

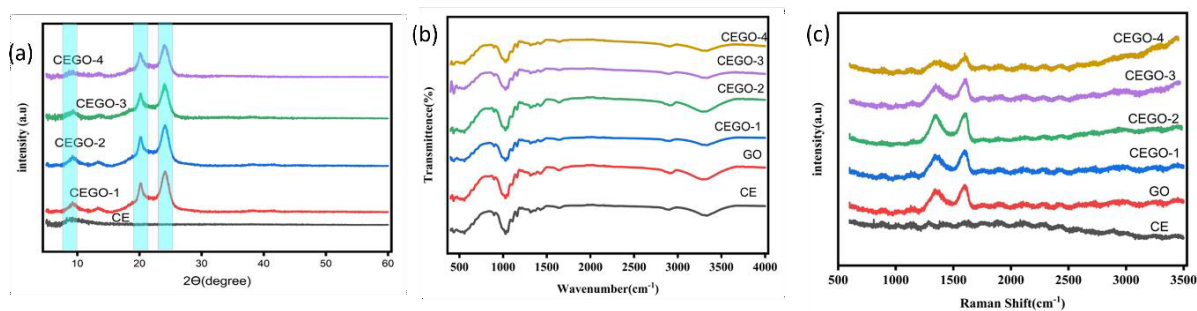


Figure 5.2. (a) XRD, (b) FTIR, (C) Raman spectroscopy of the modified membrane

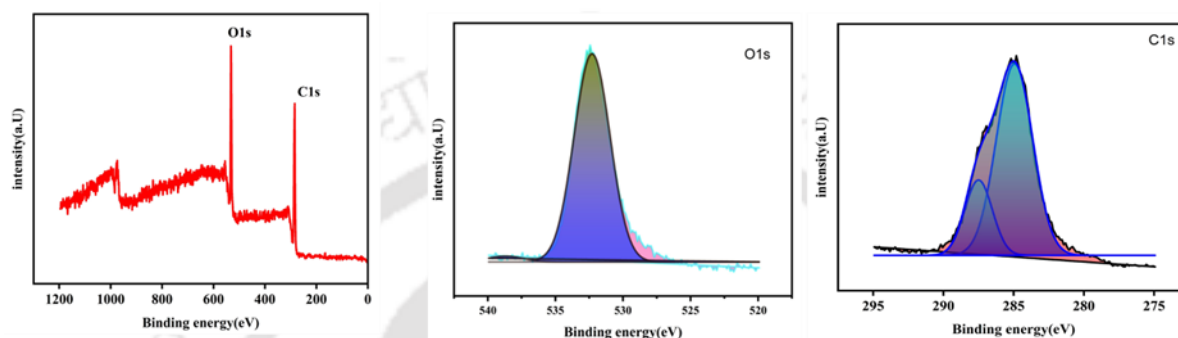


Figure 5.3. XPS spectra of modified Cellulose ether membrane

5.2.3. Mechanical and thermal stability of the fabricated membrane

The mechanical characteristics of membranes used in microbial fuel cells (MFCs) are essential for maintaining their stability under operating stressors. The study examined the impact of incorporating graphene oxide (GO) on the mechanical characteristics of pristine cellulose ether membranes by evaluating their tensile strength (TS) and elongation at break (EAB), which were measured at 20.69 ± 0.6 and $1.2 \pm 0.02\%$, respectively, as seen in **Figure 5.4 (a)**. However, with the inclusion of graphene oxide into the CE matrix (CEGO-3), the TS rose to about 2.53 times, resulting in a value of 52.3 ± 1.5 and a flexibility of 5.2 ± 0.1 , as seen in **Figure 5.4 (b)**. Comparable observations are being noted [447] [61] [62]. The incorporation of graphene oxide into CE matrices has been shown to alter the mechanical characteristics of the resulting membrane, mostly due to the unique molecular interactions formed between the graphene material and the polymer chains. This behaviour is attributed to the strong interfacial connections formed between GO and the cellulose network, particularly via hydrogen-bonding interactions that reinforce the overall matrix structure [450] [64] [450]. The enhancement

results from the robust, interconnected 3D structure formed by GO inside the cellulose matrix, which improves stress distribution and restricts polymer chain mobility. At high GO loadings, the excessive integration of nanosheets may result in structural discontinuities or weak interfacial regions, causing a progressive decline in tensile strength. This pattern aligns with the behaviour of several nanofillers, whereby an ideal concentration enhances mechanical integrity, but excessive quantities may compromise matrix consistency and reduce performance [452]. The thermogravimetric analysis was done to evaluate the thermal change after modification of the membrane to determine the thermal stability of the membrane used as a charge separator in MFC. The TGA curve in **Figure 5.4 (c)** shows that both membranes exhibit an initial weight loss of 2.7% below 100 °C, which is due to the volatilisation and vaporisation of water [453]. However, in the continuous heating run, additional mass loss was observed in the case of the CE and modified CEGO membrane, where 50 wt% reduction (T_{50}) at 179 °C to 479 °C was observed. Similarly, T_{90} mass loss for pristine CE was observed in 296 °C and 461°C. Similar has been observed in [454].

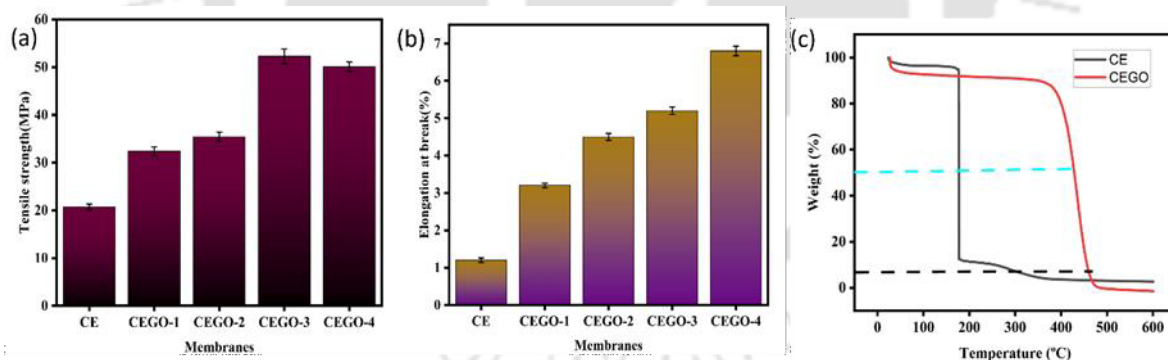


Figure 5.4. (a) Tensile strength, (b) Elongation at break of the pristine and modified membrane, (c) TGA analysis of modified and pristine CE

5.2.4. Micropollutant removal efficiency and columbic efficiency

A series of MFCs was conducted under uniform circumstances with differing amounts of Ampicillin (AMP). Ampicillin (AMP) is one of the commonly detected antibiotics in hospital effluent, which typically ranges from 1-50µg/L depending on antibiotic consumption patterns and discharge conditions. Kulkarni et al. (2017) reported an ampicillin concentration of 42µg/L

in wastewater treatment plant effluent [35]. The ampicillin concentration was determined by UV-visible spectrophotometry. A standard stock solution was prepared after calibration, and measurement was carried out at the characteristic wavelength of 230 nm. In this study a known concentration of AMP was introduced externally in the MFC anode chamber to evaluate its removal under controlled experimental conditions. This approach was adopted due to the viability of antibiotic concentrations in real hospital wastewater. **Figure 5.5 (a)** depicts the AMP removal efficiency at several concentrations (15, 25, 35, and 45 mg/L) using three different membrane-based MFCs, with AMP functioning as the antibiotic substrate with a reaction time of 70 hours. An AMP-free MFC was used as the control reactor, and the AMP removal efficiency was observed to decrease with increasing AMP concentration. At an AMP concentration of 15 mg/L, the removal efficiencies were 75.4% for MFC-A, 72.4% for MFC-B, and 63.8% for MFC-C. Upon increasing the AMP concentration to 45 mg/L, the efficiencies decreased to 55.7% (MFC-A), 51.6% (MFC-B), and 44.9% (MFC-C). Zhou et al. (2018) demonstrated a similar trend, revealing that microbial fuel cells had decreased antibiotic removal efficacy at increased concentrations across several antibiotic classes [64]. S. J. Huang et al. achieved a similar result, demonstrating that the efficacy of norfloxacin removal in microbial fuel cells diminished with increasing antibiotic concentration [65]. Similarly, when the concentration of ampicillin (AMP) increased, the degradation efficiency of the microbial population initially decreased. The anodic bacteria gradually adapted to increased AMP concentrations, exhibiting considerable tolerance and maintaining efficient activity even at 45 mg/L. This indicates that the microorganisms developed resistance due to antibiotic stress, enhancing sustained degradation effectiveness [66] [67]. An alternative hypothesis is that the oxygen-containing functional groups on the GO-modified membrane augment surface hydrophilicity and provide active adsorption sites that engage with ampicillin molecules by hydrogen bonding, π - π stacking, and electrostatic attraction. These interactions enhance antibiotic adsorption and augment its bioavailability for microbial breakdown at the anode.

Previous research has reported similar findings, indicating that negatively charged pollutants in membrane bioreactors (MBRs) demonstrated electrostatic repulsion when conductive membranes served as cathodes, hence affecting pollutant removal efficiency [68], [69]. Moreover, the effectiveness of organic matter removal, quantified by COD decrease, was assessed. The MFCs processing wastewater exhibited an initial COD of 1253 mg/L and a DO of 7.2 mg/L at 25 °C. With the escalation of ampicillin (AMP) concentration from 15 mg/L to 45 mg/L, the COD removal efficiency diminished from 96.6% to 90.2% in MFC-A, from 94.7% to 89.5% in MFC-B, and from 95.4% to 88.6% in MFC-C, as shown in **Figure 5.5 (b)**. The presence of ampicillin in the wastewater hindered microbial activity, thereby decreasing the breakdown efficiency of organic matter in the anode compartment. Similar has been observed in [67]. Previous investigations have also shown that direct exposure to high antibiotic doses might incapacitate or eliminate bacterial cells, leading to a substantial reduction in the COD removal rate [70]. The efficacy of COD removal is contingent upon the appropriate ratio of anode surface area to reactor volume and the successful migration of microorganisms from the effluent to the anode surface. **Figure 5.6 (a) & (b)** depicts the AMP and COD removal efficiency with time at a concentration of 15 mg/L using three distinct MFC designs. Significant discrepancies were noted throughout the systems over the first 5 hours. It illustrates that the GO-modified membrane-based MFC attained the greatest AMP removal efficiency of 96.3% and a COD removal efficiency of 96.2% at the maximum HRT of 70 hours. Evaluating Ampicillin diffusion in the laboratory-constructed CEGO membrane-based MFC was essential owing to a functional anode-to-cathode fuel crossover chamber, influencing MFC performance [71]. The coulombic efficiencies for the membrane-based MFCs were documented as 59.3% (MFC-C) > 56.1% (MFC-B) > 55.7% (MFC-A), as shown in **Figure 5.7**. Coulombic efficiency indicates the efficient use of the substrate for current generation throughout ten operating cycles [72]. The significant rise in coulombic efficiency demonstrates that the incorporation of ampicillin substantially improves energy recovery from the MFC system [73]. The augmented

coulombic efficiency (CE) seen in the GO-modified membrane-based MFC is mostly ascribed to improved electron recovery and decreased substrate loss, resulting from superior interfacial and membrane properties.

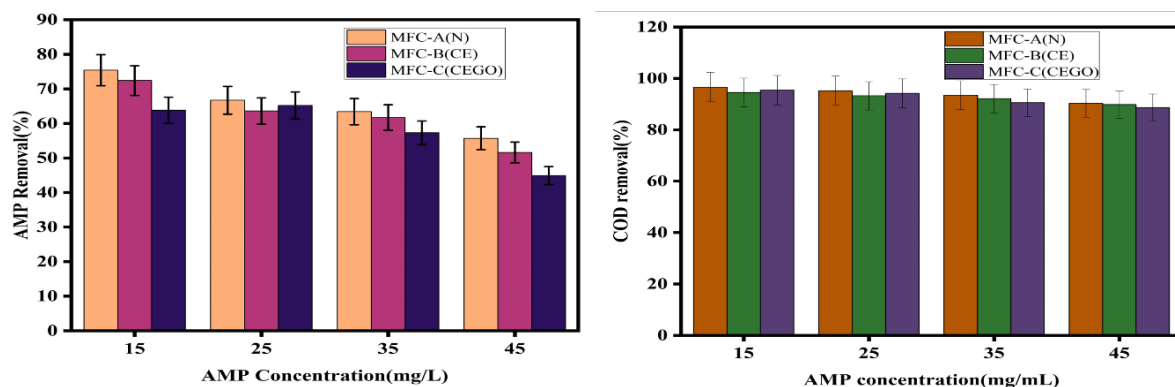


Figure 5.5.(a) Ampicillin removal, (b) COD removal efficiency through three MFCs using the fabricated membrane

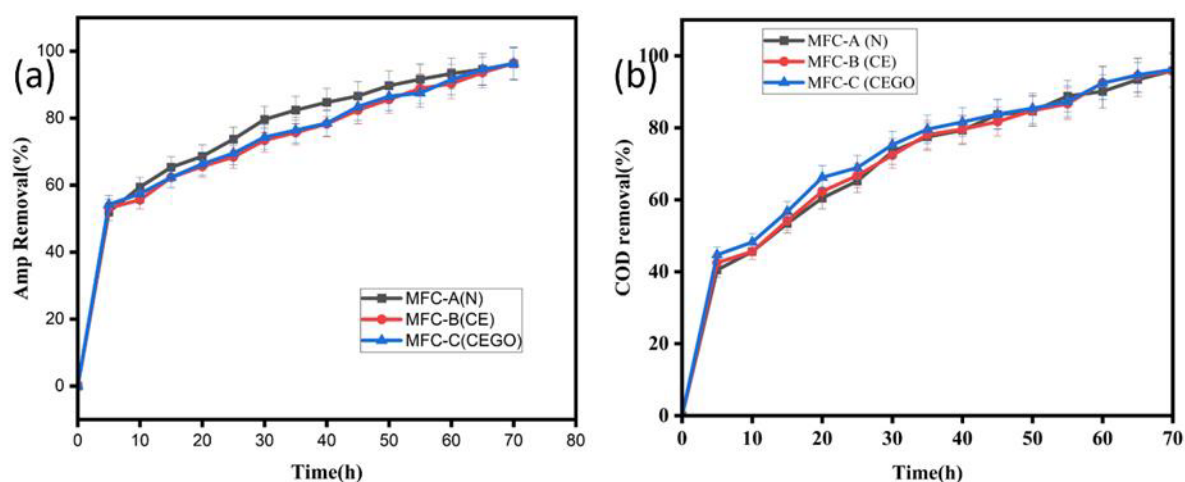


Figure 5.6. (a) AMP removal, (b) COD removal with different modified membrane-based MFCs

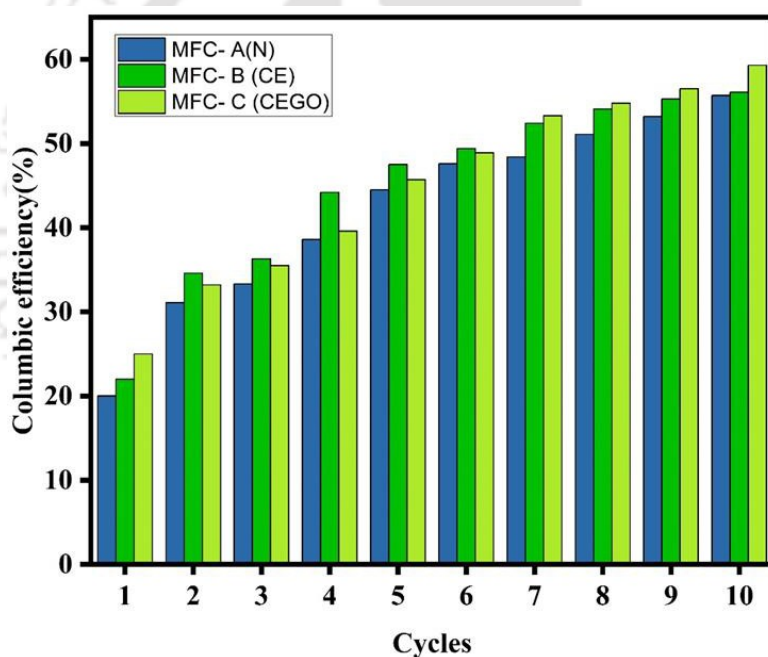


Figure 5.7. Columbic efficiency of the fabricated MFCs

5.2.5. Substrate crossover study of the fabricated membrane

The undesirable migration of fuel from the anode to the cathode via the separator is recognized to considerably diminish MFC performance [74]. Nafion's elevated expense, coupled with its propensity for significant substrate crossing, often renders it inappropriate for large-scale

applications. The quantification of a specific quantity of substrate transferred to the cathode chamber was conducted using the methodology described in a prior article[75]. **Table 5.2.** summarizes the membrane type, anode material surface area, volume, and substrate crossover analysis in the MFC. The membrane's thicker and more compact structure is most likely the cause of the notable reduction in substrate crossover. Since anodic bacteria continuously metabolize the substrate, reducing its availability for diffusion to the cathode, effective acetate leakage would be further reduced under real operating conditions with a functioning microbial population [76].

Table 5.2. A summary of the different membrane types used in miniature microbial fuel cells, considering factors such as anode size, surface area, type of fuel used, and how much material crosses between the chambers.

Anode volume(mL)	Anode material	Inoculum	PEM	Substrate	Substrate crossover diffusivity (Dcm ² /sec)	Ref
2.5	Carbon cloth	Mixed bacterial culture	Mediator less	Acetate	NA	[77]
50	Carbon felt	Synthetic wastewater	Nafion-117	Acetate	$0.06 \pm 0.003 \times 10^{-6}$	[78]
200	Carbon cloth	Mixed bacteria	GO-Modified PVA	Acetate	0.00412×10^{-6}	[79]
50	Carbon felt	<i>Saccharomyces cerevisiae</i>	GO-modified PVA	glucose	0.00342×10^{-6}	[80]
140	Graphite felt	Mixed culture	GO-modified cellulose ether (CEGO)	Ampicillin	$0.0064 \pm 0.004 \times 10^{-6}$	This study
140	Graphite felt	Mixed culture	CE	Ampicillin	$0.0078 \pm 0.003 \times 10^{-6}$	This study

5.2.6. Bioelectrical performance of the modified membrane-based MFCs

A multimeter was used to consistently measure the voltage produced by the integrated MFC system. Initially, the system had little potential, which escalated swiftly over time. The uninterrupted nutrient supply facilitated consistent proton transfer from the anode to the cathode and promoted the stable proliferation of electrogenic bacteria in the wastewater [81]. No notable delay in voltage production was detected during the initiation phase, suggesting effective microbial adherence to the anode surface. The graphite electrode was infected with a mixed bacterial culture derived from hospital effluent via three consecutive acclimation cycles. Under no-load circumstances, average voltages of 793 ± 0.3 mV and 657 ± 0.7 mV were observed for the GO-modified cellulose ether membrane-based MFC (MFC-C) and the Nafion-based MFC (MFC-A), respectively, as on **Table 5.3**. The GO-modified membrane-based MFC (MFC-C) exhibited superior open-circuit voltage (OCV) and current density compared to the PFAS- based commercial Nafion membrane, as shown in Table 5. 2. The increased open circuit voltage(OCV) noted in the graphene oxide-modified microbial fuel cell (MFC) highlights the membrane's effectiveness in facilitating selective proton transport and minimising undesirable substrate crossover. Cyclic voltammetry (CV) was conducted using an electrochemical analyser (CHIE60 series) to investigate the electron transport properties of the biocatalyst. The anode and cathode functioned as the working and counter electrodes, respectively, in conjunction with an Ag/AgCl (S) reference electrode. In situ cyclic voltammetry (CV) measurements, using an Ag/AgCl (S) reference electrode, were executed to monitor the temporal evolution of microbial metabolism and associated electron-transfer pathways. The GO-modified MFC (MFC-C) displayed distinct redox peaks at roughly -0.2 V and $+0.8$ V, as shown in the **Figure. 5.8** . The GO-modified membrane-based MFC had a peak current density of 86.6 mA/cm², which was obtained from measured voltage across varying external resistance using Ohm's law when processing complicated hospital wastewater. The

corresponding current density was obtained by normalizing current with the electrode surface area. Similar results have been reported by Li et al. (2024) and Liu Chunmei et al. (2022) [36] [37]. The proton exchange membrane (PEM) is essential in microbial fuel cell (MFC) design, functioning as a physical barrier between the anolyte and catholyte chambers and as a selective pathway for proton (H^+) transport to the cathode. The proton transfer is essential for preserving electroneutrality and completing the electrical circuit by equilibrating electron flow along the external channel. Electrochemical impedance spectroscopy (EIS) was used to assess the internal resistance of microbial fuel cells (MFCs) with different membrane configurations. **Figure 5.9** (a) presents the Nyquist curve aligned with the equivalent circuit model $R(CR)(CR)O$, precisely representing the impedance response of the MFC system. This model consists of a solution or series resistance (R_s), two parallel RC components, and an open Warburg element (O) to tackle diffusion-related issues [84]. The first RC component (R_1-C_1) of this design denotes the resistance and double-layer capacitance associated with the electrode and electrolyte interface at the anode, reflecting the initial charge transfer and ion accumulation processes. The second RC component (R_2-C_2) represents the charge transfer resistance (R_{ct}) and interfacial capacitance at the cathode or membrane electrolyte interface, indicating the efficiency of proton migration and electrochemical reduction processes. The open Warburg element (O) characterises the diffusion resistance arising from the mass transport limitations of ions inside the electrolyte or across the membrane [85]. A shortened semicircular arc in the Nyquist plot, as seen in **Figures 5.9(b) and (c)**, signifies a lower R_{ct} , suggesting expedited electron transfer kinetics and improved interfacial activity. The fitted circuit (**Figure 5.9(d)**) reveals that the GO-modified membrane-based MFC exhibited lower charge transfer resistance and decreased diffusion impedance compared to the commercial Nafion-based MFC, thereby confirming superior proton conductivity, enhanced electrode-membrane interaction, and improved electrochemical performance. The overall conversion efficiency decreases due to

various losses that hinder electron transfer between the biocatalyst and the anode. Activation losses, arising from the kinetics of bio-electrochemical reactions at the electrode interface, typically decrease as electron flow within the circuit increases [86]. Electrons generated during substrate degradation have activation losses when passing through the biocatalyst, the anode, and ultimately the cathode, due to various kinetic and interfacial impediments encountered throughout the process [87]. The activation barriers that the responding species or biocatalyst must overcome in biochemical and bio-electrochemical processes are very comparable.

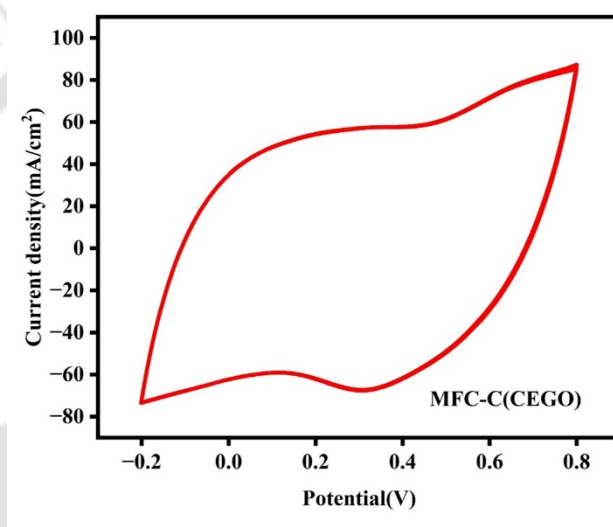


Figure 5.8. Cyclic voltammetry of GO-modified membrane-based MFCs

Table 5.3. Properties of the modified membrane-based MFCs

Membrane	MFC- A (N)	MFC-B (CE)	MFC-C (CEGO)
Maximum open circuit potential (mV)	657±0.7	786±0.5	793±0.3
Maximum current density (mA/cm²)	8.7	23.15	86.6
Coulombic efficiency (%)	55.7	56.1	59.3
R_s (Ω)	127	157.8	83
R_{ct} (Ω)	4.2	3.9	1.7

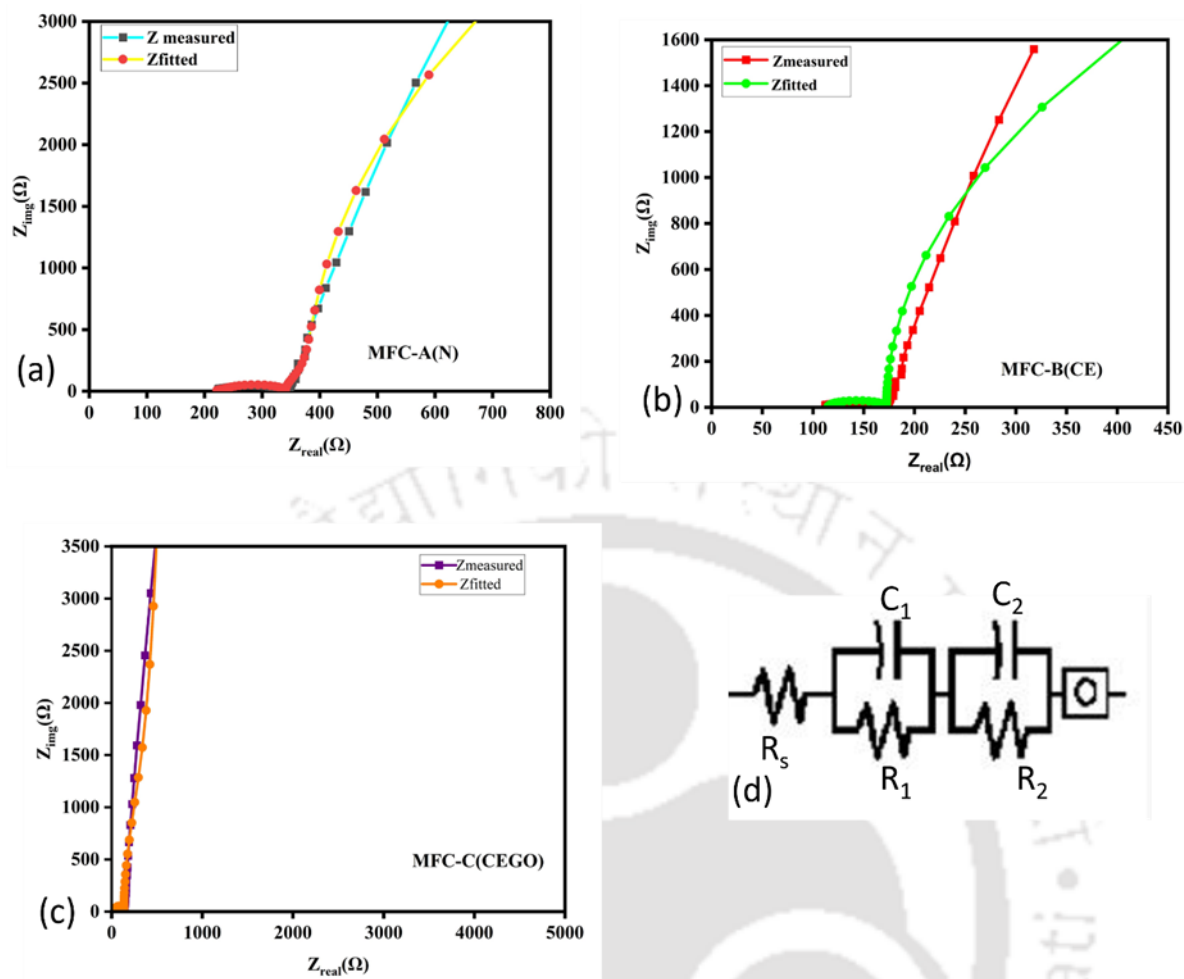


Figure 5.9. Nyquist plot (a) PFAS membrane-based, (b) pristine CE-based, (c) GO-modified CE membrane-based MFCs, (d) equivalent circuit of the EIS

5.2.7. Analysis of Bacterial Biofilm

The formation of the electroactive biofilm occurs in three phases: initial cell adherence to the electrode surface, biofilm maturation, and subsequent separation. The conductivity of the biofilm, determined by its structure and microbial composition, is crucial for power production. FESEM pictures **Figure 5.10 (a)** show the unaltered graphite felt electrode without biofilm development. **Figure 5.10 (b)** illustrates that the mixed microbial population forms a thick and organised biofilm on the electrode surface. Bacterial cells are linked by hair-like structures called pili, which stabilise the biofilm structure and function as conductive nanowires, enabling efficient electron transfer from microbial cells to the anode [90] [91].

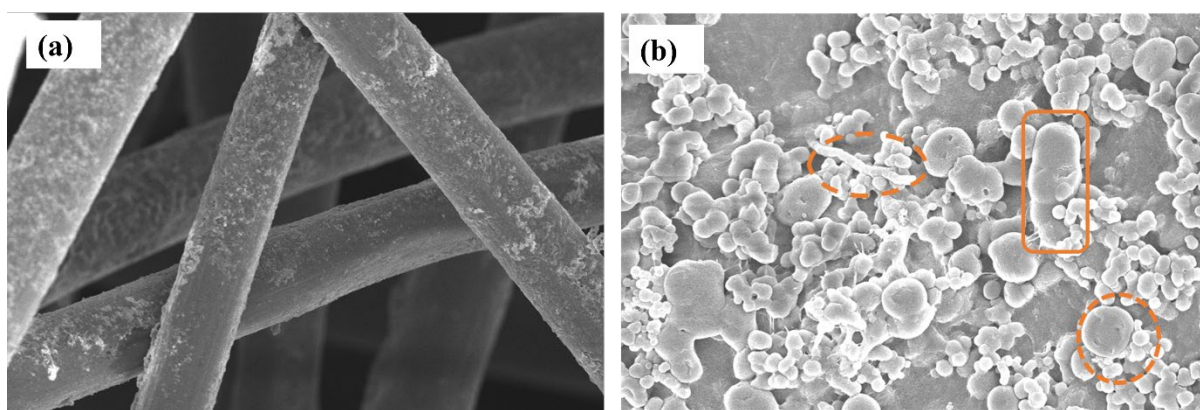


Figure 5.10. SEM image of (a) electrode without biofilm, (b) bacterial biofilm formation on electrode

5.2.8. Antimicrobial activity and surface roughness of the modified membrane

Biofouling is a significant challenge in Microbial Fuel Cell (MFC) technology, as it refers to the undesirable accumulation of microorganisms and their extracellular polymeric substances (EPS) on surfaces. In an MFC, this is a particularly problematic property, especially when it occurs on the proton exchange membrane (PEM) or the cathode. The most critical impact is an increase in the MFC's internal resistance. The biofilm layer that forms on the membrane acts as a physical barrier, obstructing the free movement of protons (H^+ ions) from the anode to the cathode. This significantly increases the ohmic resistance of the system, which in turn leads to a substantial decrease in the overall power output and efficiency. Membrane biofouling may be alleviated mainly by two strategies: (i) the anti-adhesive method, which inhibits bacterial adhesion to the membrane surface, and (ii) the antimicrobial method, which promotes the inactivation or demise of bacterial cells on the membrane. As observed in the FESEM image **Figure. 5.11 (a)**, the surface morphology of the CEGO membrane. Additionally, rupturing of the cells is being observed in **Figure. 5.11 (b)**, which was originally rod-shaped. Similar is being observed in [94], [95]. This is due to the incorporation of GO into the cellulose membrane; its two-dimensional nanosheets provide a surface that actively combats bacterial adhesion and proliferation, thereby decreasing biofouling [96]. Interestingly, in **Figure 5.11 (C)**, lytic activity

of the E coli cell was also observed, which ultimately leads to rupturing of the cell walls, which is due to GO contains numerous oxygen-containing functional groups, which can generate reactive oxygen species (ROS). Similar is being observed in the literature [97], [98]. **Figure 5.11 (d)** shows the morphology of the pristine CE membrane, whereas aggregations of bacterial cells are observable on its surface (**Figure. 5.11 (e)**), presumably due to the enhanced hydrophilicity offering more advantageous locations for microbial adherence. A similar observation is observed in [99]. These highly reactive compounds provoke significant oxidative stress in bacteria, impairing vital cellular constituents such as proteins, lipids, and DNA [100]. Utilising these properties, GO-modified cellulose membranes serve as both a physical barrier and an active agent against bacteria that seek to establish a biofilm, significantly contributing to their efficacy in reducing biofouling and improving the performance of the modified cellulose membrane assembled MFC. The surface topography of the membrane is being investigated using AFM, as shown in **Figure 5.12**. which shows that little change in surface roughness is observed by modifying the membrane with a variable quantity of GO. CEGO-3 exhibits the optimal surface roughness (RMS ~ 170.1 nm) compared to the other three modified ones. The augmented surface roughness results in an expanded surface area, and only a significant quantity of GO is appropriate in membrane modifications; otherwise, it may alter the properties of the membrane, which may hamper for fuel cell applications. Consequently, a minimal quantity of GO is appropriate for fabrication; otherwise, an excessive amount may modify its characteristics, which might be detrimental to MFC performance. Furthermore, the topography of the membrane surface is critical, since roughness significantly influences the fouling process [101], [102].

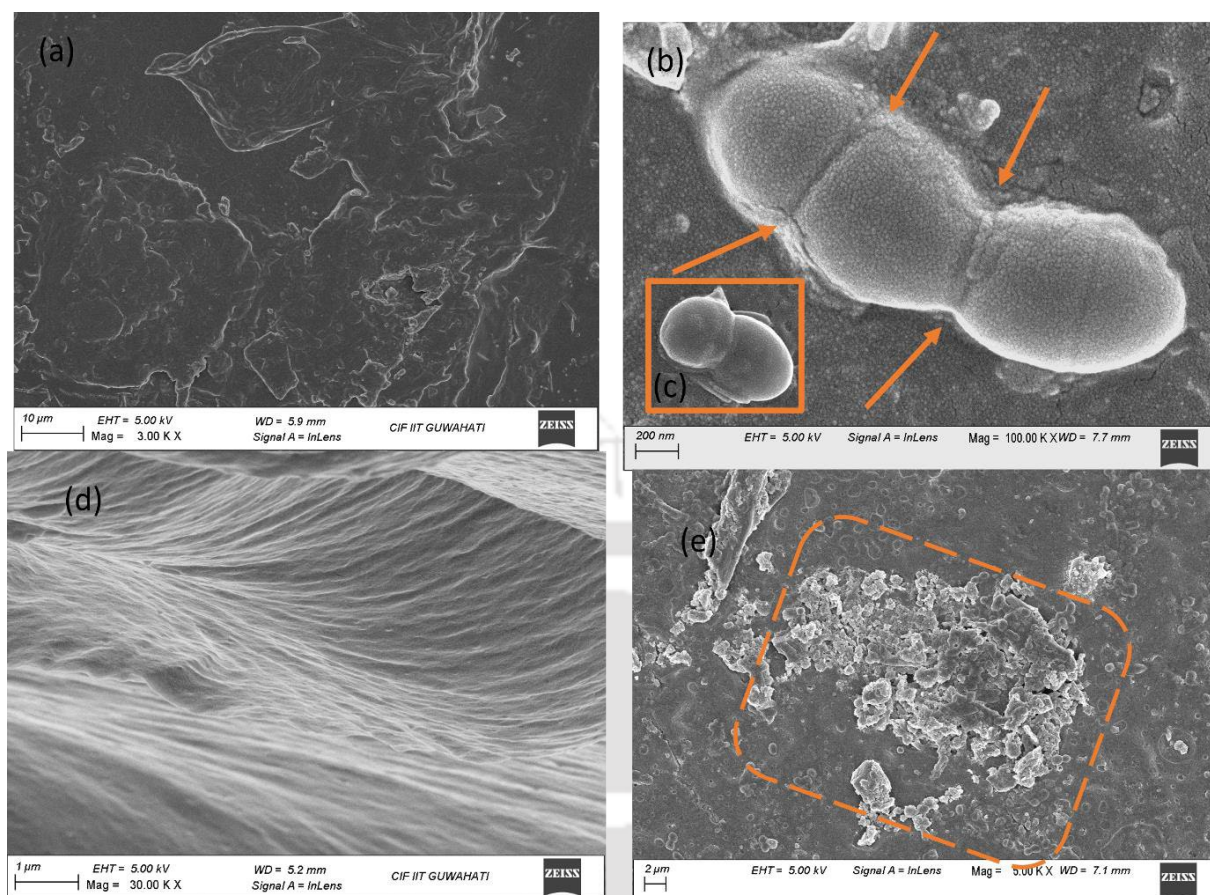


Figure 5.11. Surface morphology of (a) GO modified cellulose membrane before antimicrobial testing, (b) magnified image shows the damaging impact of the bacteria on the GO modified cellulose membrane, (c) lytic phase of the bacteria, (d) surface morphology of the unmodified cellulose membrane before antimicrobial testing, (e) cluster of bacteria formation on unmodified cellulose membrane.

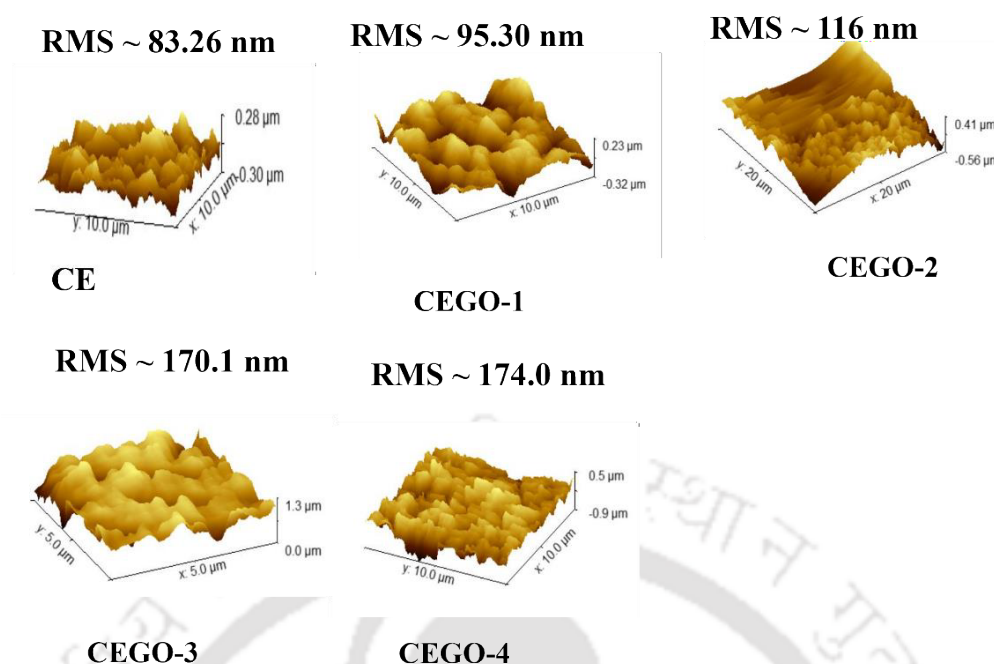


Figure 5.12. AFM analysis of the fabricated and pristine membrane

5.3. Conclusions

This work shows that graphene oxide modified cellulose ether CEGO membranes provide a viable PFAS-free option for microbial fuel cell (MFC) applications, allowing the concurrent elimination of ampicillin and the recovery of bioelectricity from wastewater. The integration of GO significantly enhanced the membrane's physicochemical characteristics, including hydrophilicity, mechanical stability with 2.53 times increased tensile strength as compared to the pristine one, and decreased substrate crossover. Consequently, on the addition of GO to the CE membrane, an optimum surface hydrophilicity has been achieved as confirmed by contact angle analysis. Additionally, the modified fabricated membrane exhibited antifouling properties as confirmed by the antibacterial study of the membrane through FESEM. Notwithstanding the elevated COD load and intricate composition of hospital wastewater, the GO-modified membrane-based MFC attained a peak current density of 86.6 mA cm^{-2} , a figure equivalent to or surpassing that documented in analogous MFC systems. This performance is significantly higher than that obtained using a PFAS-based Nafion membrane, clearly indicating the superior electrochemical efficiency and improved substrate utilization capability

of the graphene oxide–modified cellulose ether membrane. All three MFCs have exhibited almost similar removal efficiency which is due to extended reaction time of 70 hours when the microbial community was fully capable of degrading the substrate. However, MFC-C achieved an ampicillin removal efficiency of 96.3% and exhibited improved electrochemical performance, reflected by a higher coulombic efficiency of 59.3% compared to the other membrane-based MFC-A and MFC-C. In addition, the study demonstrates bio-based lab-fabricated membrane as a viable alternative to PFAS-based commercial membrane, which is more sustainable and cost-effective for practical application. The system demonstrated consistent long-term performance, reflecting structural and chemical resilience under real wastewater conditions. These findings highlight the dual environmental advantages of GO-modified cellulose ether membranes: effective mitigation of an emerging pharmaceutical contaminant and sustainable energy generation from wastewater sources. The CEGO membrane acts as a viable, eco-friendly, and cost-effective alternative to conventional PFAS-based membranes, promoting the development of safer and more sustainable MFC technologies in decentralised water treatment and resource recovery systems.

Chapter-6

Concluding Remarks and Future Prospects

6.1. Concluding Remarks

Microbial Fuel Cells (MFCs) are innovative bioelectrochemical devices that can simultaneously generate electricity and remediate wastewater. In the anodic chamber, electrogenic bacteria oxidize organic pollutants in wastewater, resulting in the degradation of hazardous contaminants and substantial decreases in chemical oxygen demand (COD). The structural design and configuration of a microbial fuel cell (MFC) are crucial in influencing its efficiency for energy recovery and organic matter removal. A microbial fuel cell (MFC) generally has an anode and a cathode, which are separated by a membrane or a membrane-less structure, allowing electroactive microorganisms to oxidize organic substrates anaerobically at the anode. The configuration, dimensions, inter-electrode spacing, and separator type significantly affect electron transfer efficiency, internal resistance, and substrate accessibility, hence directly influencing power production. Similarly, reactor design influences mass transfer, microbial adhesion, and the surface area accessible for biofilm proliferation, and also determines the rate of pollutant breakdown. Advanced micro-scaled MFC setups have been developed to decrease costs, streamline operations, and enhance scalability while maintaining treatment efficacy. Consequently, optimizing MFC design is essential for improving both the bioelectrochemical conversion of organic matter into power and the overall efficacy of wastewater cleanup. The implementation of a heart-shaped flow channel in both the anode and cathode of a miniaturized microbial fuel cell significantly enhances system performance, particularly in the treatment of actual wastewater. This unique design produces a natural mixing effect, akin to the circulation of blood within the heart. A microcontroller-driven smart data-

logging system offers a budget-friendly and smart solution for tracking MFC performance, a clear step up from expensive digital multimeters. Unlike a multimeter, which only provides manual, sporadic readings, this embedded system allows for constant monitoring during the startup and microbial acclimation phases. The employment of PFAS-free, biopolymer-based proton exchange membranes, exemplified by crosslinked poly (vinyl alcohol) (PVA), represents a notable progression in the development of sustainable microbial fuel cells (MFCs) at the micron scale. In contrast to commercially available PFAS-based PEMs, such as Nafion, which present environmental challenges, crosslinked PVA provides a non-toxic, biodegradable, and economically viable option that does not detract from functional efficacy. Its specifically engineered hydrophilicity and proton-conductive pathways facilitate effective proton transport while simultaneously mitigating oxygen and substrate crossover, which is a critical element in improving coulombic efficiency and energy recovery. Experimental findings indicate that the micro-MFC's PVA-based separator achieved a current density of 13.85 mA/cm^2 and a coulombic efficiency of 85.5%, thereby suggesting its considerable capacity for energy generation. Moreover, the system's COD removal efficiency, measured at $68\% \pm 0.10\%$, underscored its efficacy in wastewater treatment applications. An antibacterial composite membrane, synthesised via a green-solvent approach, presents a significant advancement for energy recovery from hospital wastewater within microbial fuel cells (MFCs). The composite CA-CS membrane-based MFC, when fed with real wastewater, exhibited a maximum exchange current density of 1.2 mA/m^2 , a result of the low charge transfer resistance of 3.8Ω , as confirmed through EIS analysis. This diminished resistance indicates enhanced electrochemical reactions, heightened catalytic performance, and more efficient electron transfer between the microbial biofilm and the electrode interface.

6.2. Future Scope

This research opens up several ways to improve micro-scale microbial fuel cell (MFC) technology. Future studies could focus on scaling up the heart-like microfluidic design into modular arrays. This would allow for greater power output and the treatment of larger amounts of wastewater. Evaluating the long-term stability and removal efficiency of new contaminants, like antibiotics and other micropollutants, can be improved by applying this method to real hospital and pharmaceutical wastewater. Moreover, if the engineering of future wastewater-fed microbial fuel cells (MFCs) systems can facilitate hydrogen production, it will substantially enhance overall energy recovery. This approach would yield a more valuable and cleaner fuel product when contrasted with direct electricity generation. Incorporation of a booster circuit for voltage multiplication and a storage device is one of the important aspects. Finally, life cycle assessments can also be useful to evaluate commercial feasibility, sustainability benefits, and potential industrial adoption.

References

- [1] M. Al Sharabati, R. Abokwiek, ... A. A.-O.-E., "Biodegradable polymers and their nano-composites for the removal of endocrine-disrupting chemicals (EDCs) from wastewater: A review," *Environ Res.* 2021 Nov;202:111694. doi: 10.1016/j.envres.2021.111694. Epub 2021 Jul 15. PMID: 34274334
- [2] F. Karimi, A. Ayati, B. Tanhaei, A. Sanati, S. A.-E, "Removal of metal ions using a new magneticchitosan nano-bio-adsorbent; A powerful approach in water treatment," *Environ Res.* 2022 Jan;203:111753. doi: 10.1016/j.envres.2021.111753. Epub 2021 Jul 28. PMID: 34331923.
- [3] F. O.-M. Journal of social sciences, "Water pollution: sources, effects, control and management," (2013). *Mediterranean Journal of Social Sciences*, 4(8), 65.
- [4] F. Chaudhry, M. M.-J. Ecosyst. Ecography, "Factors affecting water pollution: a review *EcosystEcography* in 2017 (Vol 7, Page 225) doi: 10.4172/2157-7625.1000225.
- [5] R. P. Schwarzenbach, T. Egli, T. B. Hofstetter, U. Von Gunten, and B. Wehrli, "Global waterpollution and human health," *annualreviews.org*, vol. 35, pp. 109–136, Nov. 2010, doi: 10.1146/ANNUREV-ENVIRON-100809-125342.
- [6] C. Author *et al.*, "The environmental risk and water pollution: A review from the river basins around the world," *Journal of Sustainable Agriculture*, 2013, vol. 7, no. 2, pp. 126–136.
- [7] H. Karimi-Maleh, A. Ayati, R. Davoodi, ... B. T.-J. of C., "Recent advances in using of chitosan- based adsorbents for removal of pharmaceutical contaminants: A review," *Journal of CleanerProduction*, 291, 125880.
- [8] H. Karimi-Maleh, A. Ayati, S. Ghanbari, Y. O.-J. of molecular, and undefined 2021, "Recent advances in removal techniques of Cr (VI) toxic ion from aqueous solution: A comprehensive review," *Journal of molecular liquids*, 329, 115062.
- [9] H. Karimi-Maleh, M. Shafieizadeh, M. T. "The role of magnetite/graphene oxide nano-composite as a high-efficiency adsorbent for removal of phenazopyridine residues from water samples, an experimental/theoretical investigation." *Journal of Molecular Liquids* 298 (2020): 112040
- [10] M. Varsha, P. Senthil Kumar, and B. Senthil Rathi, "A review on recent trends in the removal of emerging contaminants from aquatic environment using low-cost adsorbents," *Chemosphere*, vol. 287, Jan. 2022, doi: 10.1016/J.CHEMOSPHERE.2021.132270.
- [11] A. Sengupta, M. Jebur, M. Kamaz, and S. R. Wickramasinghe, "Removal of EmergingContaminants from Wastewater Streams Using Membrane Bioreactors: A Review,"*Membranes (Basel)*, vol. 12, no. 1, Jan. 2022, doi: 10.3390/MEMBRANES12010060.
- [12] M. Priyadarshini, I. Das, M. M. Ghangrekar, and L. Blaney, "Advanced oxidation processes: Performance, advantages, and scale-up of emerging technologies," *J Environ Manage*, vol. 316, Aug. 2022, doi: 10.1016/J.JENVMAN.2022.115295.
- [13] Noguera-Oviedo, Katia, and Diana S. Aga. "Lessons learned from more than two decades of research on emerging contaminants in the environment." *Journal of hazardous materials* 316 (2016): 242-251.

- [14] M. Petrovic *et al.*, “Emerging contaminants in waste waters: sources and occurrence,” vol. 5 S1, pp. 1–35, 2008, doi: 10.1007/698_5_106.
- [15] J. L. Domingo, “Health risks of dietary exposure to perfluorinated compounds,” *Environ Int*, vol. 40, no. 1, pp. 187–195, 2012, doi: 10.1016/J.ENVINT.2011.08.001.
- [16] M. Chaturvedi, A. Mishra, K. Sharma, G. Sharma, G. Saxena, and A. K. Singh, “Emerging contaminants in wastewater: sources of contamination, toxicity, and removal approaches,” *Springer Emerging treatment technologies for waste management, 2021* pp. 103–132, Jan. 2021, doi: 10.1007/978-981-16-2015-7_5.
- [17] S. Khan, L. Aijun, S. Zhang, Q. Hu, Y. Z.-J. of hazardous materials, “Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation,” *Journal of hazardous materials*, 152(2), 506-515.
- [18] H. W.-J. of E. Sciences and undefined 2007, “Treated wastewater irrigation effect on soil, crop and environment: Wastewater recycling in the loess area of China,” *Journal of Environmental Sciences*, 19(9), 1093-1099.
- [19] H. Ajwa, M. T.-B. and F. of Soils, “Decomposition of different organic materials in soils,” *Springer HA Ajwa, MA Tabatabai Biology and Fertility of Soils*, vol. 18, no. 3, pp. 175–182, Sep. 1994, doi: 10.1007/BF00647664.
- [20] M. Johns, J. B.-S. S. S. of America, “Root zone leachate from high chemical oxygen demand cannery water irrigation,” vol. 71, no. 6, pp. 1893–1901, Nov. 2007, doi: 10.2136/SSSAJ2007.0063.
- [21] M. Raud, T. Kikas, O. Sippula, and N. J. Shurpali, “Potentials and challenges in lignocellulosic biofuel production technology,” *Renewable and Sustainable Energy Reviews*, vol. 111, pp. 44–56, Sep. 2019, doi: 10.1016/J.RSER.2019.05.020.
- [22] L. E. Mitchell *et al.*, “Long-term urban carbon dioxide observations reveal spatial and temporal dynamics related to urban characteristics and growth,” *Proc Natl Acad Sci U S A*, vol. 115, no. 12, pp. 2912–2917, Mar. 2018, doi: 10.1073/PNAS.1702393115
- [23] J. A. Albarracin-Arias, C. P. Yu, T. Maeda, W. Valdivieso Quintero, and V. Sanchez-Torres, “Microbial community dynamics and electricity generation in MFCs inoculated with POME sludges and pure electrogenic culture,” *Int J Hydrogen Energy*, vol. 46, no. 74, pp. 36903–36916, Oct. 2021, Doi: 10.1016/J.IJHYDENE.2021.08.218.
- [24] S. T. Oh, “Trend of Mathematical Models in Microbial Fuel Cell for Environmental Energy Refinery from Waste/Water,” *Springer Proceedings in Physics*, vol. 135, pp. 25–30, 2010, doi: 10.1007/978-3-642-13624-5_3.
- [25] E. Emmanuel, M. Pierre, Y. P.-E. International, “Groundwater contamination by microbiological and chemical substances released from hospital wastewater: Health risk assessment for drinking water, assessment for drinking water consumers” *Environment international*, 35(4), 718-726
- [26] M. Al Aukidy, P. Verlicchi, N. V.-S. of the T. Environment, “A framework for the assessment of the environmental risk posed by pharmaceuticals originating from hospital effluents,” *Science of the Total Environment*, 493, 54-64.

- [27] M. Al Aukidy, S. Al Chalabi, P. V. -, undefined management, treatment “Hospital wastewatertreatments adopted in Asia, Africa, and Australia,” vol. 60, pp. 171–188, 2018, doi: 10.1007/698_2017_5.
- [28] Datta, P., Mohi, G., & Chander, J. (2018). Biomedical waste management in India: Criticalappraisal. *Journal of laboratory physicians*, 10(01), 006-014.
- [29] P. Verlicchi, M. Al Aukidy, E. Z. “What have we learned from worldwide experiences on themanagement and treatment of hospital effluent An overview and a discussion on perspectives,” *Science of the Total Environment*, 514 (2015): 467-491
- [30] K. Timraz, Y. Xiong, H. Al Qarni, P. H.-S. W. R. &, “Removal of bacterial cells, antibiotic resistance genes and integrase genes by on-site hospital wastewater treatment plants:surveillane of treated hospital effluent,” *Environmental Science: Water Research & Technology*, 3(2), 293-303
- [31] Verlicchi, P., Al Aukidy, M., & Zambello, E. (2015). What have we learned from worldwideexperiences on the management and treatment of hospital effluent?—An overview and adiscussion on perspectives. *Science of the Total Environment*, 514, 467-491.
- [32] Mestre, A. S., Campinas, M., Viegas, R. M., Mesquita, E., Carvalho, A. P., & Rosa, M. J. (2022).Activated carbons in full-scale advanced wastewater treatment. *Advanced materials for sustainable environmental remediation*, 433-475.
- [33] A. Watkinson, E. Murby, D. K. “The occurrence of antibiotics in an urban watershed: fromwastewater to drinking water,” *Science of the total environment*, 407(8), 2711-2723.
- [34] K. Timraz, Y. Xiong, H. Al Qarni, and P. Y. Hong, “Removal of bacterial cells, antibiotic resistancegenes and integrase genes by on-site hospital wastewater treatment plants: surveillane of treated hospital effluent quality,” *Environ Sci (Camb)*, vol. 3, no. 2, pp. 293–303, Mar. 2017, Doi: 10.1039/C6EW00322B.
- [35] B. C. Iweriebor, S. Gaqavu, L. C. Obi, U. U. Nwodo, and A. I. Okoh, “Antibiotic Susceptibilities ofEnterococcus Species Isolated from Hospital and Domestic Wastewater Effluents in Alice, Eastern Cape Province of South Africa,” *International Journal of Environmental Research and Public Health* 2015, Vol. 12, Pages 4231-4246, vol. 12, no. 4, pp. 4231–4246, Apr. 2015, doi: 10.3390/IJERPH120404231.
- [36] Chartier, Yves, ed. *Safe management of wastes from health-care activities*. World Health Organization, 2014.
- [37] J. P. Zotesso, E. S. Cossich, V. Janeiro, and C. R. G. Tavares, “Treatment of hospital laundry wastewater by UV/H2O2 process,” *Environmental Science and Pollution Research*, vol. 24, no.7, pp. 6278–6287, Mar. 2017, doi: 10.1007/S11356-016-6860-5.
- [38] Emmanuel, E., Perrodin, Y., Keck, G., Blanchard, J. M., & Vermande, P. (2005). Ecotoxicologicalrisk assessment of hospital wastewater: a proposed framework for raw effluents discharginginto urban sewer network. *Journal of hazardous materials*, 117(1), 1-11.
- [39] Carraro, E., Bonetta, S., Bertino, C., Lorenzi, E., Bonetta, S., & Gilli, G. (2016). Hospital effluentsmanagement: chemical, physical, microbiological risks and legislation in different countries. *Journal of environmental management*, 168, 185-199.

- [40] Carraro, E., Bonetta, S., Bertino, C., Lorenzi, E., Bonetta, S. and Gilli, G., 2016. Hospital effluents management: chemical, physical, microbiological risks and legislation in different countries. *Journal of environmental management*, 168, pp.185-199.
- [41] “Mishra: A study: biomedical waste management in India - Google Scholar.” Accessed: Nov.12, 2025.
- [42] Carraro, Elisabetta, et al. "Hospital effluents management: chemical, physical, microbiological risks and legislation in different countries." *Journal of environmental management* 168 (2016): 185-199.
- [43] L. Kovalova, H. Siegrist, H. Singer, A. Wittmer, and C. S. McArdell, “Hospital Wastewater Treatment by Membrane Bioreactor: Performance and Efficiency for Organic Micropollutant Elimination,” *Environ Sci Technol*, vol. 46, no. 3, pp. 1536–1545, Feb. 2012, doi: 10.1021/ES203495D.
- [44] A. P. M. Velenturf and P. Purnell, “Principles for a sustainable circular economy,” *Sustain Prod Consum*, vol. 27, pp. 1437–1457, Jul. 2021, doi: 10.1016/J.SPC.2021.02.018.
- [45] S. B. Pasupuleti, S. Srikanth, X. Dominguez-Benetton, S. V. Mohan, and D. Pant, “Dual gasdiffusion cathode design for microbial fuel cell (MFC): optimizing the suitable mode of operation in terms of bioelectrochemical and bioelectro-kinetic evaluation,” *Journal of Chemical Technology & Biotechnology*, vol. 91, no. 3, pp. 624–639, Mar. 2016, doi: 10.1002/JCTB.4613.
- [46] Y. Tao *et al.*, “Fluorescent probe based subcellular distribution of Cu(II) ions in living electrotrophs isolated from Cu(II)-reduced biocathodes of microbial fuel cells,” *Bioresour Technol*, vol. 225, pp. 316–325, Feb. 2017, doi: 10.1016/J.BIORTECH.2016.11.084.
- [47] H. Hiegemann *et al.*, “An integrated 45 L pilot microbial fuel cell system at a full-scale wastewater treatment plant,” *Bioresour Technol*, vol. 218, pp. 115–122, Oct. 2016, doi: 10.1016/J.BIORTECH.2016.06.052.
- [48] E. Marsili, D. B. Baron, I. D. Shikhare, D. Coursolle, J. A. Gralnick, and D. R. Bond, “Shewanellasecretes flavins that mediate extracellular electron transfer,” *Proceedings of the National Academy of Sciences*, vol. 105, no. 10, pp. 3968–3973, Mar. 2008, doi: 10.1073/PNAS.0710525105.
- [49] R. Selvasembian *et al.*, “Recent progress in microbial fuel cells for industrial effluent treatment and energy generation: Fundamentals to scale-up application and challenges,” *Bioresour Technol*, vol. 346, p. 126462, Feb. 2022, doi: 10.1016/J.BIORTECH.2021.126462.
- [50] M. Ahanchi *et al.*, “Review on waste biomass valorization and power management systems for microbial fuel cell application,” *J Clean Prod*, vol. 380, p. 134994, Dec. 2022, doi: 10.1016/J.JCLEPRO.2022.134994.
- [51] P. Singh, A. Srivastava, N. Srivastava, N. Sinha, V. Sharma, and A. Upadhyay, “Microbial fuel cellas innovative approach for bio-electricity generation: A review,” *Materials Protection*, vol. 65,no. 3, pp. 426–439, 2024, doi: 10.62638/ZASMAT1184.
- [52] A. Gherghel, C. Teodosiu, and S. De Gisi, “A review on wastewater sludge valorisation and its challenges in the context of circular economy,” *J Clean Prod*, vol. 228, pp. 244–263, Aug. 2019,doi: 10.1016/J.JCLEPRO.2019.04.240.

- [53] R. H. Mahmoud, O. M. Gomaa, and R. Y. A. Hassan, "Bio-electrochemical frameworks governing microbial fuel cell performance: technical bottlenecks and proposed solutions," *RSC Adv*, vol. 12, no. 10, pp. 5749–5764, Feb. 2022, doi: 10.1039/D1RA08487A.
- [54] D. Shindell and C. J. Smith, "Climate and air-quality benefits of a realistic phase-out of fossil fuels," *Nature*, vol. 573, no. 7774, pp. 408–411, Sep. 2019, doi: 10.1038/S41586-019-1554-Z;SUBJMETA.
- [55] V. K. M Das, O Zandraa, C Mudenur, N Saha, P Saha, B Mandal, "Composite scaffolds based on bacterial cellulose for wound dressing application," *ACS Appl Bio Mater*, vol. 8, pp. 3722–3733, 2022, doi: <https://doi.org/10.1021/acsabm.2c00226>.
- [56] V. K. K Mondal, P Bhagabati, VV Goud, S Sakurai, "Utilization of microalgae residue and isolated cellulose nanocrystals: A study on crystallization kinetics of poly (ϵ -caprolactone) bio-composites," *Int J Biol Macromol*, vol. 191, pp. 521–530, 2021, doi: <https://doi.org/10.1016/j.ijbiomac.2021.09.114>.
- [57] V. K. M Das, B Mandal, "Sustainable routes for synthesis of poly (ϵ -caprolactone): Prospects in chemical industries," 2020. doi: http://dx.doi.org/10.1007/978-981-15-1251-3_2.
- [58] E. Q. S. Angioni, L. Millia, G. Bruni, C. Tealdi, P. Mustarelli, "Improving the performances of NafionTM-based membranes for microbial fuel cells with silica-based, organically- functionalized mesostructured fillers," *J power sources*, vol. 334, pp. 120–127, 2016.
- [59] R. P. Arvind Gupta, Akhilesh Kumar Pal and P. D. and V. Katiyar, "Green composites films with excellent barrier properties," in *Advanced Green Composites*, 2018, p. 321. doi: <http://dx.doi.org/10.1002/9781119323327.ch12>.
- [60] Md. M. R. Sadia Sikder, "Efficiency of microbial fuel cell in wastewater (municipal, textile and tannery) treatment and bioelectricity production," *case studies in chemical and environmental Engineering*, vol. 8, p. 100421, 2023, doi: <https://doi.org/10.1016/j.cscee.2023.100421>.
- [61] V. K. SS Borkotoky, T Ghosh, "Biodegradable Nanocomposite Foams: Processing, Structure, and Properties," in *Advances in Sustainable Polymer*, 2020. doi: https://doi.org/10.1007/978-981-15-1251-3_12.
- [62] C. W. S. F.R. Dowdy, R. Kawakita, M. Lange, "Meta-analysis of microbial fuel cells using waste substrates," *Appl. Biochem. Biotechnol*, vol. 185, pp. 221–232, 2018, doi: <https://doi.org/10.1007/s12010-017-2652-8>.
- [63] R. M. F. de Fouchécour, V. Larzillière, T. Bouchez, "Systematic and quantitative analysis of two decades of anodic wastewater treatment in bioelectrochemical reactors," *Water Res*, vol. 214, p. 118142, 2022, doi: <https://doi.org/10.1016/j.watres.2022.118142>.
- [64] V. K. J Bindu, K Sathish Kumar, SK Panda, "Biopolymer Dispersed Poly Lactic Acid Composites and Blends for Food Packaging Applications," in *Advances in Sustainable Polymers: Processing and Applications*, 2019, pp. 209–235. doi: https://doi.org/10.1007/978-981-32-9804-0_10.
- [65] L. H. Li Z, Yao L, Kong L, "Electricity generation using a baffled microbial fuel cell convenient for stacking," *Bioresour. Technol*, vol. 99, pp. 1650–1655, 2008, doi: <https://doi.org/10.1016/j.biortech.2007.04.003>.

- [66] B. C. Dekker A, Heijne AT, Saakes M, Hamelers HVM, "Analysis and improvement of a scaled-up and stacked microbial fuel cell," *Energy Environ.Sci*, vol. 43, pp. 9038–9042, 2009, doi: <https://doi.org/10.1021/es901939r>.
- [67] S. Y. M.M. Mardanpour, "Characterization of a microfluidic microbial fuel cell as a power generator based on a nickel electrode," *Biosens. Bioelectron*, vol. 79, pp. 327–333, 2016, doi: <https://doi.org/10.1016/j.bios.2015.12.022>.
- [68] Et. al Dian Anggraini, Nobutoshi Ota, Yigang Shen, "Recent advances in microfluidic devices for single-cell cultivation: methods and applications," *Lab Chip*, vol. 22, pp. 1438–1468, 2022, doi: <https://doi.org/10.1039/D1LC01030A>.
- [69] F. Johnsson, J. Kjärstad, and J. Roozen, "The threat to climate change mitigation posed by the abundance of fossil fuels," *Climate Policy*, vol. 19, no. 2, pp. 258–274, Feb. 2019, doi: 10.1080/14693062.2018.1483885.
- [70] I. Gajda, J. Greenman, and I. A. Ieropoulos, "Recent advancements in real-world microbial fuel cell applications," *Curr Opin Electrochem*, vol. 11, pp. 78–83, Oct. 2018, doi: 10.1016/J.COEELEC.2018.09.006.
- [71] K. Sri Lakshmi and M. Anji Reddy, "Wastewater – An overview," *International Journal of Contemporary Research and Review*, vol. 8, no. 8, pp. 20254–20262, Aug. 2017, doi: 10.15520/ijcrr/2017/8/08/287.
- [72] C. Liu, H. Lin, B. Li, Y. Dong, and T. Yin, "Responses of microbial communities and metabolic activities in the rhizosphere during phytoremediation of Cd-contaminated soil," *Ecotoxicology and Environmental Safety*, vol. 195, Art. no. 110438, 2020, doi: 10.1016/j.ecoenv.2020.110438.
- [73] R. Kaur, S. Wani, A. Singh, ... K. L. the 2nd regional workshop on, and undefined 2012, "Wastewater production, treatment and use in India," *academia. Dur Kaur, SP Wani, AK Singh, K Lal. National Report presented at the 2nd regional workshop on Safe Use of, 2012•academia.edu*, Accessed: Aug. 15, 2025.
- [74] V. Dhawan, "Water and agriculture in India: background paper for the South Asia expert panel during the Global Forum for Food and Agriculture (GFFA) 2017," 2017, Accessed: Aug. 15, 2025. [Online]. Available: https://epub.sub.uni-hamburg.de/epub/frontdoor.php?source_opus=75897&la=de
- [75] A. O. Fayiga, M. O. Ipinmoroti, and T. Chirenje, "Environmental pollution in Africa," *Springer Environment, development and sustainability*, 2018 vol. 20, no. 1, pp. 41–73, Feb. 2018, doi: 10.1007/S10668-016-9894-4.
- [76] N. Akhtar, M. S. Ishak, S. Bhawani, K. U.- Water, and undefined 2021, "Various natural and anthropogenic factors responsible for water quality degradation: A review," Aug. 15, 2025.
- [77] A. Majumder, A. Gupta, P. Ghosal, M. V.-J. of environmental, and undefined 2021, "A review on hospital wastewater treatment: A special emphasis on occurrence and removal of pharmaceutically active compounds, resistant microorganisms," *Elsevier Majumder, AK Gupta, PS Ghosal, M Varma Journal of environmental chemical engineering, 2021•Elsevier*, Accessed: Aug. 15, 2025.
- [78] N. Diaz-Elsayed, N. Rezaei, T. Guo, ... S. M.-R., and undefined 2019, "Wastewater-based resource recovery technologies across scale: a review," *Elsevier Diaz-Elsayed, N Rezaei, T Guo, S Mohebbi, Q Zhang Resources, Conservation and Recycling, 2019•Elsevier*, Accessed: Aug. 15, 2025.

- [79] A. Paruch, T. Mæhlum, R. Eltun, E. Tapu, O. S.-E. Engineering, and undefined 2019, "Green wastewater treatment technology for agritourism business in Romania," *Spin Ecological Engineering*, 2019 <https://www.sciencedirect.com/science/article/pii/S0925857419302277>
- [80] V. W. Callewaert P, Aelterman P, Pham TH, De Schamphelaire L, Carballa M, Rabaey K, "Minimizing losses in bio-electrochemical systems: the road to applications.," *Appl Microbiol Biotechnol*, vol. 79, pp. 901–913, 2008, doi: <https://doi.org/10.1007/s00253-008-1522-2>.
- [81] Y. Z. Zihui Lin, Dagang Li, "Energy efficiency of lithium-ion batteries: Influential factors and long-term degradation," *J Energy Storage*, vol. 74, p. 109386, 2023, doi: <https://doi.org/10.1016/j.est.2023.109386>.
- [82] A. T. G. L. Theofilos Kamperidis, "Architecture Optimization of a Single-Chamber Air-Cathode MFC by Increasing the Number of Cathode Electrodes," *Sustainability*, vol. 15, p. 13107, 2023, doi: <https://doi.org/10.3390/su151713107>.
- [83] Shanhue Jiang, Haishu Sun, Huijiao Wang, et al. Al, "A comprehensive review on the synthesis and applications of ion exchange membranes," *Chemosphere*, vol. 282, 2021, doi: <https://doi.org/10.1016/j.chemosphere.2021.130817>.
- [84] Cristina Pozo-Gonzalo, Kate Nairn, et al. "An investigation of commercial carbon air cathode structure in ionic liquid-based sodium oxygen batteries," *Sci Rep*, vol. 10, 2020, doi: <https://doi.org/10.1038/s41598-020-63473-y>.
- [85] Z. H. L. Xiao, Z. Ge, P. Kelly, F. Zhang, "Evaluation of normalised energy recovery (NER) in microbial fuel cells affected by reactor dimensions and substrates," *Bioresour. Technol*, vol. 157, pp. 77–83, 2014, doi: <https://doi.org/10.1016/j.biortech.2014.01.086>.
- [86] Z. H. Z. Wang, "Demystifying terms for understanding bioelectrochemical systems towards sustainable wastewater treatment," *Curr. Opin. Electrochem*, vol. 19, pp. 14–19, 2020, doi: <https://doi.org/10.1016/j.coelec.2019.09.001>.
- [87] Hien Nguyen, Florian Lombeck, Claudia Schwarz, Philipp A. Heizmann, et al. "Hydrocarbon-based Pemion TM proton exchange membrane fuel cells with state-of-the-art performance," *Sustainable Energy Fuels*, vol. 5, pp. 3687–3699, 2021, doi: <https://doi.org/10.1039/D1SE00556A>.
- [88] G. H.-F. J. Ramirez-Nava, M. Martínez-Castreón, R.L. García-Mesino, J.A. López-Díaz, O. Talavera-Mendoza, A. Sarmiento-Villagrana, F. Rojano, "The Implications of Membranes Used as Separators in Microbial Fuel Cells," *Membranes (Basel)*, vol. 11, p. 738, 2021, doi: <https://doi.org/10.3390/membranes11100738>.
- [89] A. A. Z. M. Shabani, H. Younesi, M. Pontié, A. Rahimpour, M. Rahimnejad, "A critical review on recent proton exchange membranes applied in microbial fuel cells for renewable energy recovery," *J Clean Prod*, vol. 264, p. 121446, 2020, doi: <https://doi.org/10.1016/j.jclepro.2020.121446>.
- [90] S. D. P.N. Venkatesan, "Effect of cation transport of SPEEK – rutile TiO₂ electrolyte on microbial fuel cell performance," *J Membr Sci*, vol. 492, pp. 518–527, 2015, doi: <https://doi.org/10.1016/j.memsci.2015.06.025>.
- [91] S. e. a. S. et al, "Highly efficient sulfonated polybenzimidazole as a proton exchange membrane for microbial fuel cells," *J Power Sources*, vol. 317, 2016.
- [92] P. P. R. Rudra, V. Kumar, N. Pramanik, P.P. Kundu, "Graphite oxide incorporated crosslinked polyvinyl alcohol and sulfonated styrene nanocomposite membrane as

- separating barrier insingle chambered microbial fuel cell,” *j power sources*, vol. 341, pp. 285–293, 2017, doi: <https://doi.org/10.1016/j.jpowsour.2016.12.028>.
- [93] Z. R. S. Zinadini, A.A. Zinatizadeh, M. Rahimi, V. Vatanpour, “High power generation and CODremoval in a microbial fuel cell operated by a novel sulfonated PES/PES blend proton exchange membrane,” *Energy*, vol. 125, pp. 427–438, 2017, doi: <https://doi.org/10.1016/j.energy.2017.02.146>.
- [94] S. K. H. Ilbeygi, M. Ghasemi, D. Emadzadeh, A.F. Ismail, S.M.J. Zaidi, S.A. Aljlil, J. Jaafar, D. Martin, “Power generation and wastewater treatment using a novel SPEEK nanocomposite membrane in a dual chamber microbial fuel cell,” *Int J Hydrogen Energy*, vol. 40, pp. 477–487, 2015, doi: <https://doi.org/10.1016/j.ijhydene.2014.10.026>.
- [95] B. R. Md. T. N. M. M. G. Tiwari, “A novel low cost polyvinyl alcohol-Nafion-borosilicate membrane separator for microbial fuel cell,” *Material chemistry and physycs*, vol. 182, pp. 86–93, 2016, doi: <http://dx.doi.org/10.1016%2Fj.matchemphys.2016.07.008>.
- [96] Y. G. Q. Xu, L. Wang, Chen Li, X. Wang, Cuicui Li, “Study on improvement of the protonconductivity and anti-fouling of proton exchange membrane by doping SGO@SiO₂ in microbial fuel cell applications,” *Int J Hydrogen Energy*, vol. 44, p. 15322, 2019, doi: <https://doi.org/10.1016/j.ijhydene.2019.03.238>.
- [97] J. Ma, Z. Wang, D. Suor, S. Liu, J. Li, and Z. Wu, “Temporal variations of cathode performancein air-cathode single-chamber microbial fuel cells with different separators,” *J Power Sources*, vol. 272, pp. 24–33, Dec. 2014, doi: 10.1016/J.JPOWSOUR.2014.08.053.
- [98] V. Kumar, P. Kumar, A. Nandy, and P. P. Kundu, “A nanocomposite membrane composed of incorporated nano-alumina within sulfonated PVDF-co-HFP/Nafion blend as separating barrier in a single chambered microbial fuel cell,” *RSC Adv*, vol. 6, no. 28, pp. 23571–23580, Feb. 2016, doi: 10.1039/C6RA03598A.
- [99] V. Kumar, S. Mondal, A. Nandy, and P. P. Kundu, “Analysis of polybenzimidazole and polyvinylpyrrolidone blend membranes as separating barrier in single chambered microbialfuel cells,” *Biochem Eng J*, vol. 111, pp. 34–42, Jul. 2016, doi: 10.1016/J.BEJ.2016.03.003.
- [100] M. Hosseini, I. A.-J. of P. Sources, and undefined 2012, “A dual-chambered microbial fuel cellwith Ti/nano-TiO₂/Pd nano-structure cathode,” *Elsevier Hosseini, I Ahadzadeh Journal of Power Sources*, 201Apr. 25, 2025.
- [101] V. Kumar, P. Kumar, A. Nandy, P. K.-R. Advances, and undefined 2016, “Fabrication of laminated and coated Nafion 117 membranes for reduced mass transfer in microbial fuel cells,” *RSC Advances*, 2016 vol. 6, no. 26, pp. 21526–21534, 2016, doi: 10.1039/c6ra02234k.
- [102] J. X. Leong, W. R. W. Daud, M. Ghasemi, A. Ahmad, M. Ismail, and K. Ben Liew, “Composite membrane containing graphene oxide in sulfonated polyether ether ketone in microbial fuelcell applications,” *Int J Hydrogen Energy*, vol. 40, no. 35, pp. 11604–11614, Sep. 2015, doi: 10.1016/J.IJHYDENE.2015.04.082.
- [103] M. M. G. B.R. Tiwari, M.T.T. Noori, “A novel low-cost polyvinyl alcohol-Nafion-borosilicate membrane separator for microbial fuel cell,” *Mater. Chem. Phys.*, vol. 182, pp. 86–93, 2016,doi: <https://doi.org/10.1016/j.matchemphys.2016.07.008>.
- [104] A. F. I. S. Shahgaldi, M. Ghasemi, W.R. Wan Daud, Z. Yaakob, M. Sedighi, J. Alam, “Performanceenhancement of microbial fuel cell by PVDF/Nafion nanofiber composite proton exchange membrane,” *Fuel Process. Technol*, vol. 124, pp. 290–295, 2014, doi:

<https://doi.org/10.1016/j.fuproc.2014.03.015>.

- [105] S.-H. R. G. Palanisamy, H.-Y. Jung, T. Sadhasivam, M.D. Kurkuri, S.C. Kim, “A comprehensive review on microbial fuel cell technologies: processes, utilisation, and advanced developments in electrodes and membranes,” *J Clean Prod*, vol. 221, pp. 598–621, 2019, doi: <https://doi.org/10.1016/j.jclepro.2019.02.172>.
- [106] S.-H. R. H.-Y. Jung, “Polyvinylidene Fluoride Nanofiber Composite Membrane Coated with Perfluorinated Sulfuric Acid for Microbial Fuel Cell Application,” *J. Nanosci. Nanotechnol.*, vol. 20, pp. 5711–5715, 2020, doi: <https://doi.org/10.1166/jnn.2020.17622>.
- [107] S.-H. P. B. Roshanravan, H. Younesi, M. Abdollahi, M. Rahimnejad, “Application of proton-conducting sulfonated polysulfone incorporated MIL-100(Fe) composite materials for polymer-electrolyte membrane microbial fuel cells,” *J Clean Prod*, vol. 300, p. 126963, 2021, doi: <https://doi.org/10.1016/j.jclepro.2021.126963>.
- [108] M. A. S.J. Peighambaroust, S. Rowshanzamir, “Review of the proton exchange membranes for fuel cell applications,” *Int J Hydrogen Energy*, vol. 35, pp. 9349–9384, 2010AD, doi: <https://doi.org/10.1016/j.ijhydene.2010.05.017>.
- [109] S. V. V. M. S. Singha, T. Jana, J.A.A. Modestra, A. Naresh Kumar, “Highly efficient sulfonated polybenzimidazole as a proton exchange membrane for microbial fuel cells,” *j power sources*, vol. 317, pp. 143–152, 2016, doi: <https://doi.org/10.1016/j.jpowsour.2016.03.103>.
- [110] R. S. A.A. Olayiwola Sirajudeen, M.S. Mohamad Annuar, K.A. Ishak, H. Yusuf, “Innovative application of biopolymer composite as proton exchange membrane in microbial fuel cell utilizing real wastewater for electricity generation,” *J. Clean. Prod.*, vol. 278, 2021, doi: <https://doi.org/10.1016/j.jclepro.2020.123449>.
- [111] C. S. F. C. Vilela, A.C. Silva, E.M. Domingues, G. Gonçalves, M.A. Martins, F.M. Figueiredo, S.A. Santos, “Conductive polysaccharides-based proton-exchange membranes for fuel cell applications: The case of bacterial cellulose and fucoidan,” *Carbohydr. Polym.*, vol. 230, p. 115604, 2020, doi: <https://doi.org/10.1016/j.carbpol.2019.115604>.
- [112] P. S. L. Wang, X. Zuo, A. Raut, R. Isseroff, Y. Xue, Y. Zhou, B. Sandhu, T. Schein, T. Zeliznyak, “Operation of proton exchange membrane (PEM) fuel cells using natural cellulose fiber membranes,” *Sustainable Energy Fuels*, vol. 3, pp. 2725–2732, 2019, doi: <https://doi.org/10.1039/C9SE00381A>.
- [113] S. G. U.S. Jayapiriya, “Influence of cellulose separators in coin-sized 3D printed paper-based microbial fuel cells,” *Sustainable Energy Technol. Assess.*, vol. 47, p. 101535, 2021, doi: <https://doi.org/10.1016/j.seta.2021.101535>.
- [114] N. Y. S. Muhmed, N.A.M. Nor, J. Jaafar, A. Ismail, M. Othman, M.A. Rahman, F. Aziz, “Emerging chitosan and cellulose green materials for ion exchange membrane fuel cell: a review,” *Energy Ecol. Environ*, vol. 5, pp. 85–107, 2020, doi: <https://doi.org/10.1007/s40974-019-00127-4>.
- [115] S. Y. Ma J, “Chitosan biopolymer for fuel cell applications. Carbohydr Polym.,” *Carbohydr Polym.*, pp. 955–975., 2013, doi: <https://doi.org/10.1016/j.carbpol.2012.10.015>.
- [116] F. S. M. Mashkour, M. Rahimnejad, M. Mashkour, “Increasing bioelectricity generation in microbial fuel cells by a high-performance cellulose-based membrane electrode assembly,”

- Appl. Energy*, vol. 282, p. 116150, 2021, doi: <https://doi.org/10.1016/j.apenergy.2020.116150>.
- [117] M. S. P. Srinophakun, A. Thanapimmetha, S. Plangsri, S. Vetchayakunchai, "Application of modified chitosan membrane for microbial fuel cell: Roles of proton carrier site and positive charge," *J Clean Prod*, vol. 142, pp. 1274–1282, 2017, doi: <https://doi.org/10.1016/j.jclepro.2016.06.153>.
- [118] M. M. G. I. Chakraborty, S. Das, B.K. Dubey, "Novel low-cost proton exchange membrane made from sulphonated biochar for application in microbial fuel cells," *Mater. Chem. Phys.*, vol. 239, p. 122025, 2020, doi: <https://doi.org/10.1016/j.matchemphys.2019.122025>.
- [119] S. B. D. Vidhyeswari, A. Surendhar, "Enhanced performance of novel carbon nanotubes - sulfonated poly ether ether ketone (speek) composite proton exchange membrane in mfc application," *Chemosphere*, vol. 293, 2022, doi: <https://doi.org/10.1016/j.chemosphere.2022.133560>.
- [120] Et. al Tahernia, Mehdi, Ellie Plotkin-Kaye, Maedeh Mohammadifar, Yang Gao, "Characterization of Electrogenic Gut Bacteria," *ACS Omega*, vol. 45, 2020, doi: <https://doi.org/10.1021%2Facsomega.0c04362>.
- [121] B. L. A, X. Z. A, F. G. A, W. W. B, and T. Z. A, "Characterization of tetracycline resistant bacterial community in saline activated sludge using batch stress incubation with high-throughput sequencing analysis," *Water Res*, pp. 4207–4216, 2013, doi: <http://dx.doi.org/10.1016/j.watres.2013.04.021>.
- [122] Paquete CM, "Electroactivity across the cell wall of Gram-positive bacteria," *Compt struct Biotechnol .J*, vol. 18, pp. 3796–3802, 2020, doi: <https://doi.org/10.1016%2Fj.csbj.2020.11.021>.
- [123] H. Xu, X. L. Yang, Z. H. Zhang, Y. G. Xia, and H. L. Song, "External circuit loading mode regulates anode biofilm electrochemistry and pollutants removal in microbial fuel cells," *Bioresour Technol*, vol. 410, p. 131300, Oct. 2024, doi: [10.1016/J.BIORTECH.2024.131300](https://doi.org/10.1016/J.BIORTECH.2024.131300).
- [124] S. J. You, Q. L. Zhao, J. Q. Jiang, J. N. Zhang, and S. Q. Zhao, "Sustainable approach for leachate treatment: Electricity generation in microbial fuel cell," *J Environ Sci Health A Tox Hazard Subst Environ Eng*, vol. 41, no. 12, pp. 2721–2734, Dec. 2006, doi: [10.1080/10934520600966284](https://doi.org/10.1080/10934520600966284).
- [125] J. Xian *et al.*, "α-FeOOH nanowires loaded on carbon paper anodes improve the performance of microbial fuel cells," *Chemosphere*, vol. 273, p. 129669, Jun. 2021, doi: [10.1016/J.CHEMOSPHERE.2021.129669](https://doi.org/10.1016/J.CHEMOSPHERE.2021.129669).
- [126] Shuxin Zhang, Shuxin Zhang, Shuxin Zhang, Lachlan Coin, et al. "Molecular Methods for Pathogenic Bacteria Detection and Recent Advances in Wastewater Analysis," *Water (Basel)*, vol. 13, p. 3551, 2021, doi: <https://doi.org/10.3390/w13243551>.
- [127] Naser Bazina, Tariq G. Ahmed, Mostafa Almdaaf, et al. al "Power generation from wastewater using microbial fuel cells: A review," *J. Biotechnol.*, vol. 374, pp. 17–30, 2023, doi: <https://doi.org/10.1016/j.jbiotec.2023.07.006>.
- [128] Jing Ren, Na Li, Maohua Du, et. al "Study on the effect of synergy between the mixed cultures on the power generation of microbial fuel cells," *Bioengineered*, vol. 12, pp. 844–854, 2021, doi: <https://doi.org/10.1080%2F21655979.2021.1883280>.

- [129] M. Shirkosh, Y. Hojjat, and M. M. Mardanpour, "Boosting microfluidic microbial fuel cells performance via investigating electron transfer mechanisms, metal-based electrodes, and magnetic field effect," *Sci Rep*, vol. 12, no. 1, Dec. 2022, doi: 10.1038/s41598-022-11472-6.
- [130] P. Falås, A. Wick, S. Castronovo, J. H.-W. research, and undefined 2016, "Tracing the limits of organic micropollutant removal in biological wastewater treatment," *Elsevier Falås, A Wick, S Castronovo, J Habermacher, TA Ternes, A Joss. Water research*, 2016•Elsevier, Accessed: Aug. 15, 2025.
- [131] F. Sariatli, "Linear Economy Versus Circular Economy: A Comparative and Analyzer Study for Optimization of Economy for Sustainability," *Visegrad Journal on Bioeconomy and Sustainable Development*, vol. 6, no. 1, pp. 31–34, May 2017, doi: 10.1515/VJBSD-2017-0005.
- [132] O. Adel Badawi Omar, F. Raed Abd Al Rahim, S. Adil Abduljabar Saed, Y. Zeyad Yassen Daoud, and A. Alrahman Mohammed Jasim Mohammed, "BIOELECTRICAL PRODUCTION BY MICROBIAL NANOWIRES," *Journal of Medical Genetics and Clinical Biology*, vol. 1, 2024, doi:10.61796/jmgcb.v1i8.833.
- [133] Y. Zhang, *Energy recovery from waste streams with microbial fuel cell (MFC)-based technologies*. DTU Environment, 2012. May 16, 2025.
- [134] K. U. Mahto and S. Das, "Electroactive biofilm communities in microbial fuel cells for the synergistic treatment of wastewater and bioelectricity generation," *Crit Rev Biotechnol*, vol. 45, no. 2, pp. 434–453, 2025, doi: 10.1080/07388551.2024.2372070.
- [135] S. Il Pyun, "Thermodynamic and electro-kinetic analyses of direct electron transfer (DET) and mediator-involved electron transfer (MET) with the help of a redox electron mediator," *Journal of Solid State Electrochemistry*, vol. 24, no. 11–12, pp. 2685–2693, Nov. 2020, doi: 10.1007/S10008-020-04780-2
- [136] F. Wang *et al.*, "Structure of Microbial Nanowires Reveals Stacked Hemes that Transport Electrons over Micrometres," *Cell*, vol. 177, no. 2, pp. 361–369.e10, Apr. 2019, doi: 10.1016/J.CELL.2019.03.029.
- [137] Z. Wang, Y. Hu, Y. Dong, L. Shi, and Y. Jiang, "Enhancing electrical outputs of the fuel cells with *Geobacter sulfurreducens* by overexpressing nanowire proteins," *Microb Biotechnol*, vol. 16, no. 3, p. 534, Mar. 2022, doi: 10.1111/1751-7915.14128.
- [138] J. M. Dantas *et al.*, "Rational engineering of *Geobacter sulfurreducens* electron transfer components: A foundation for building improved *Geobacter*-based bioelectrochemical technologies," *Front Microbiol*, vol. 6, no. JUL, 2015, doi: 10.3389/FMICB.2015.00752.
- [139] A. Hernández-Eligio, G. A. Huerta-Miranda, S. Martínez-Bahena, D. Castrejón-López, M. Miranda-Hernández, and K. Juárez, "GSU1771 regulates extracellular electron transfer and electroactive biofilm formation in *Geobacter sulfurreducens*: Genetic and electrochemical characterization," *Bioelectrochemistry*, vol. 145, Jun. 2022, doi: 10.1016/J.BIOELECHEMA.2022.108101.
- [140] H. T. Ouboter *et al.*, "Mechanisms of extracellular electron transfer in anaerobic methanotrophic archaea," *Nat Commun*, vol. 15, no. 1, Dec. 2024, doi: 10.1038/S41467-024-45758-2.

- [141] D. R. Lovley and D. E. Holmes, "Electromicrobiology: the ecophysiology of phylogenetically diverse electroactive microorganisms," *Nat Rev Microbiol*, vol. 20, no. 1, pp. 5–19, Jan. 2022, doi: 10.1038/S41579-021-00597-6.
- [142] H. Y. Yang *et al.*, "Redox mediator-modified biocathode enables highly efficient microbial electro-synthesis of methane from carbon dioxide," *Appl Energy*, vol. 274, p. 115292, Sep. 2020, doi: 10.1016/J.APENERGY.2020.115292.
- [143] X. Yin, F. Wang, M. Ge, F. Zhang, and G. Liang, "Pseudomonas aeruginosa promoted microbial fuel cells for cytidine acid production wastewater treatment," *Sci Rep*, vol. 15, no. 1, pp. 1–14, Dec. 2025, doi: 10.1038/S41598-025-90361-0
- [144] S. Kondaveeti, G. Mohanakrishna, A. Kumar, C. Lai, J. K. Lee, and V. C. Kalia, "Exploitation of Citrus Peel Extract as a Feedstock for Power Generation in Microbial Fuel Cell (MFC)," *Indian J Microbiol*, vol. 59, no. 4, pp. 476–481, Dec. 2019, doi: 10.1007/S12088-019-00829-7/FIGURES/3.
- [145] I. Chakraborty, S. M. Sathe, B. K. Dubey, and M. M. Ghangrekar, "Waste-derived biochar: Applications and future perspective in microbial fuel cells," *Bioresour Technol*, vol. 312, p. 123587, Sep. 2020, doi: 10.1016/J.BIORTECH.2020.123587.
- [146] S. Pandit *et al.*, "Agricultural Waste and Wastewater as Feedstock for Bioelectricity Generation Using Microbial Fuel Cells: Recent Advances," *Fermentation 2021, Vol. 7, Page 169*, vol. 7, no. 3, p. 169, Aug. 2021, doi: 10.3390/FERMENTATION7030169.
- [147] M. Ji *et al.*, "A biodegradable chitosan-based composite film reinforced by ramie fibre and lignin for food packaging," *Carbohydr Polym*, vol. 281, p. 119078, Apr. 2022, doi: 10.1016/J.CARBPOL.2021.119078.
- [148] Y. Qin, X. Yin, X. Xu, X. Yan, F. Bi, and W. Wu, "Specific surface area and electron donating capacity determine biochar's role in methane production during anaerobic digestion," *Bioresour Technol*, vol. 303, p. 122919, May 2020, doi: 10.1016/J.BIORTECH.2020.122919.
- [149] R. Sivaranjane, P. Senthil Kumar, B. Chitra, and G. Rangasamy, "A critical review on biochar for the removal of toxic pollutants from water environment," *Chemosphere*, vol. 360, p. 142382, Jul. 2024, doi: 10.1016/J.CHEMOSPHERE.2024.142382.
- [150] Z. Liu *et al.*, "Modified biochar: synthesis and mechanism for removal of environmental heavy metals," *Carbon Research*, vol. 1, no. 1, pp. 1–21, Dec. 2022, doi: 10.1007/S44246-022-00007-3/FIGURES/1.
- [151] S. Kumar, P. Shukla, K. Das, and V. Katiyar, "Chitosan/water caltrop pericarp extract reinforced active edible film and its efficacy as strawberry coating for prolonging shelf life," *Int J Biol Macromol*, vol. 307, p. 142115, May 2025, doi: 10.1016/J.IJBIOMAC.2025.142115.
- [152] T. Ranade, A. Sati, A. Pratap, and S. N. Mali, "Curcumin-integrated biopolymer films for active packaging: current trends and future directions," *Chemical Papers*, Mar. 2025, doi: 10.1007/S11696-025-03892-1.
- [153] M. S. Rana *et al.*, "Biological insights into alleviating heavy metal toxicity through the simultaneous supply of biochar biofilters derived from the Mikania micrantha and molybdenum nanoparticles," *Biochar*, vol. 7, no. 1, pp. 1–25, Dec. 2025, doi: 10.1007/S42773-024-00414-2/FIGURES/11.

- [154] M. Hemalatha, J. S. Sravan, B. Min, and S. Venkata Mohan, "Concomitant use of Azolla-derived bioelectrode as anode and hydrolysate as substrate for microbial fuel cell and electro-fermentation applications," *Science of The Total Environment*, vol. 707, p. 135851, Mar. 2020, doi: 10.1016/J.SCITOTENV.2019.135851.
- [155] M. Agarwal, J. Tardio, and S. V. Mohan, "Pyrolysis Biochar from Cellulosic Municipal SolidWaste as Adsorbent for Azo Dye Removal: Equilibrium Isotherms and Kinetics Analysis," *International Journal of Environmental Science and Development*, vol. 6, no. 1, pp. 67–72, 2015, doi: 10.7763/IJESD.2015.V6.563.
- [156] K. Zhang, Y. Deng, Z. Liu, Y. Feng, C. Hu, and Z. Wang, "Biochar Facilitated Direct Interspecies Electron Transfer in Anaerobic Digestion to Alleviate Antibiotics Inhibition and Enhance Methanogenesis: A Review," *Int J Environ Res Public Health*, vol. 20, no. 3, p. 2296, Feb. 2023, doi: 10.3390/IJERPH20032296.
- [157] C. Yang *et al.*, "Carbon dots-fed *Shewanella oneidensis* MR-1 for bioelectricity enhancement," *Nature Communications* 2020 11:1, vol. 11, no. 1, pp. 1–11, Mar. 2020, doi: 10.1038/s41467-020-14866-0.
- [158] A. Gemünde, B. Lai, L. Pause, J. Krömer, and D. Holtmann, "Redox Mediators in Microbial Electrochemical Systems," *ChemElectroChem*, vol. 9, no. 13, p. e202200216, Jul. 2022, doi:10.1002/CELC.202200216.
- [159] A. Gemünde, B. Lai, L. Pause, J. Krömer, and D. Holtmann, "Redox Mediators in Microbial Electrochemical Systems," *ChemElectroChem*, vol. 9, no. 13, Jul. 2022, doi: 10.1002/CELC.202200216.
- [160] E. S. Gloag, D. J. Wozniak, P. Stoodley, and L. Hall-Stoodley, "Mycobacterium abscessus biofilms have viscoelastic properties which may contribute to their recalcitrance in chronic pulmonary infections," *Sci Rep*, vol. 11, no. 1, pp. 1–8, Dec. 2021, doi: 10.1038/S41598-021-84525
- [161] S. He, L. Feng, W. Zhao, J. Li, Q. Zhao, and L. Wei, "Composition and molecular structure analysis of hydrophilic/hydrophobic extracellular polymeric substances (EPS) with impacts on sludge dewaterability," *Chemical Engineering Journal*, vol. 462, p. 142234, Apr. 2023, doi: 10.1016/J.CEJ.2023.142234.
- [162] Z. Tang, J. Yu, F. Fan, S. Wang, D. Wang, and Y. Huang, "Effects of redox-modified biochar on mercury reduction and methylation on electron transfer in *Geobacter sulfurreducens* PCA," *Bioresour Technol*, vol. 427, p. 132423, Jul. 2025, doi: 10.1016/J.BIORTECH.2025.132423.
- [163] R. Xu, Y. Fu, Y. Xu, X. Zheng, Y. X. Huang, and F. Meng, "Comparing biotransformation of extracellular polymeric substances (EPS) under aerobic and anoxic conditions: Reactivities, components, and bacterial responses," *Chemosphere*, vol. 296, p. 133996, Jun. 2022, doi: 10.1016/J.CHEMOSPHERE.2022.133996.
- [164] B. Viridis, S. T. Read, K. Rabaey, R. A. Rozendal, Z. Yuan, and J. Keller, "Biofilm stratification during simultaneous nitrification and denitrification (SND) at a biocathode," *Bioresour Technol*, vol. 102, no. 1, pp. 334–341, Jan. 2011, doi: 10.1016/J.BIORTECH.2010.06.155.
- [165] K. B. Gregory and D. R. Lovley, "Remediation and recovery of uranium from contaminated subsurface environments with electrodes," *Environ Sci Technol*, vol. 39, no. 22, pp. 8943–

- 8947, Nov. 2005, doi:
10.1021/ES050457E/SUPPL_FILE/ES050457ESI20050907_121224.PDF.
- [166] K. B. Gregory, D. R. Bond, and D. R. Lovley, "Graphite electrodes as electron donors for anaerobic respiration," *Environ Microbiol*, vol. 6, no. 6, pp. 596–604, Jun. 2004, doi: 10.1111/J.1462-
 - [167] M. Sharma *et al.*, "Bioelectrocatalyzed reduction of acetic and butyric acids via direct electron transfer using a mixed culture of sulfate-reducers drives electrosynthesis of alcohols and acetone," *Chemical Communications*, vol. 49, no. 58, pp. 6495–6497, Jun. 2013, doi: 10.1039/C3CC42570C.
 - [168] K. C. Costa *et al.*, "Protein complexing in a methanogen suggests electron bifurcation and electron delivery from formate to heterodisulfide reductase," *Proc Natl Acad Sci U S A*, vol. 107, no. 24, pp. 11050–11055, Jun. 2010, doi: 10.1073/PNAS.1003653107/SUPPL_FILE/ST03.DOC.
 - [169] W. B. Whitman, T. L. Bowen, and D. R. Boone, "The Methanogenic Bacteria," *The Prokaryotes*, pp. 165–207, 2006, doi: 10.1007/0-387-30743-5_9.
 - [170] A. Kouzuma, T. Kasai, A. Hirose, and K. Watanabe, "Catabolic and regulatory systems in *Shewanella oneidensis* MR-1 involved in electricity generation in microbial fuel cells," *Front Microbiol*, vol. 6, no. JUN, p. 149564, Jun. 2015, doi: 10.3389/FMICB.2015.00609/XML.
 - [171] H. Hassan, S. Dai, and B. Jin, "Bioelectrochemical Reaction Kinetics, Mechanisms, and Pathways of Chlorophenol Degradation in MFC Using Different Microbial Consortia," *ACS Sustain Chem Eng*, vol. 7, no. 20, pp. 17263–17272, Oct. 2019.
 - [172] C. Santoro, C. Arbizzani, B. Erable, and I. Ieropoulos, "Microbial fuel cells: From fundamental to applications. A review," *J Power Sources*, vol. 356, p. 225, 2017, doi: 10.1016/J.JPOWSOUR.2017.03.109.
 - [173] F. Johnsson, J. Kjärstad, and J. Rootzén, "The threat to climate change mitigation posed by the abundance of fossil fuels," *Taylor & Francis F Johnsson, J Kjärstad, J Rootzén Climate Policy, 2019* • Taylor & Francis, vol. 19, no. 2, pp. 258–274, Feb. 2019, doi: 10.1080/14693062.2018.1483885.
 - [174] T.-J. J. Ahmed Fuwad, Hyunil Ryu, Noah Malmstadt, Sun Min Kim, "Biomimetic membranes as potential tools for water purification: Preceding and future avenues," *Desalination*, vol. 458, pp. 97–115, 2019, doi: <https://doi.org/10.1016/j.desal.2019.02.003>.
 - [175] Et. al Xiaoyan Zhang, Pascal Tanner, Alexandra Graff, "Mimicking the cell membrane with block copolymer membranes," *Polymer Chemistry*, vol. 50, 2012, doi: <https://doi.org/10.1002/pola.26000>.
 - [176] M. Di, Alberto Tiraferri, Valentina-Elena Musteata, Valentina-Elena Musteata Vincenzo, "Biomimetic artificial water channel membranes for enhanced desalination," *Nat Nanotechnol*, vol. 16, pp. 190–196, 2021, doi: <https://doi.org/10.1038/s41565-020-00796-x>.
 - [177] Et. al Lin-Bing Zou, Jue-Ying Gong, Xiaojie Ju, "Smart membranes for biomedical applications," *Chin J Chem Eng*, vol. 49, pp. 34–45, 2022, doi: <https://doi.org/10.1016/j.cjche.2022.06.006>.
 - [178] Et. al Elvira Pantuso, Ejaz Ahmed, Enrica Fontananova, Adele Brunetti, Ibrahim Tahir, "Smart dynamic hybrid membranes with self-cleaning capability," *nature communication*,

- vol. 14, 2023, doi: <https://doi.org/10.1038/s41467-023-41446-9>.
- [179] Z. U. Yi Pan, Yapeng Liu, Shuangchun Yang, Changqing Zhang, “Sun Q. Preparation of acrylonitrile-sulfonamide copolymer ultrafiltration membrane and its anti-pollution performance, Dissertation,” *Nanotechnol Rev*, vol. 12, 2023, doi: <https://doi.org/10.1515/ntrev-2022-0538>.
- [180] et al Zhang ZL, Dong X, Fan YN, Yang LM, He L, Song F, “Chameleon-inspired variable coloration enabled by a highly flexible photonic cellulose film,” *ACS Appl Mater Interfaces*, vol. 41, pp. 1–20, 2020, doi: <https://doi.org/10.1021/acsami.0c13551>.
- [181] et al Zheng WW, Huang JY, Li SH, Ge MZ, Teng L, Chen Z, “Advanced materials with special wettability toward intelligent oily wastewater remediation,” *ACS Appl Mater Interfaces*, vol. 13, pp. 67–87, 2020, doi: <https://doi.org/10.1021/acsami.0c18794>.
- [182] H. X. T. Ying, J. Su, Y. Jiang, Q. Ke, “A pre-wetting induced superhydrophilic/superlipophilic micro-patterned electrospun membrane with self-cleaning property for on-demand emulsified oily wastewater separation,” *J. Hazard Mater.*, vol. 384, 2020, doi: <https://doi.org/10.1016/j.jhazmat.2019.121475>.
- [183] K. T. D.T. Nguyen, “A floating microbial fuel cell: Generating electricity from Japanese ricewashing wastewater,” *Energy Rep.*, vol. 6, pp. 758–762, 2020, doi: <https://doi.org/10.1016/j.egyr.2020.11.134>.
- [184] B. E. L. Y. Ahn, “Effectiveness of domestic wastewater treatment using microbial fuel cells at ambient and mesophilic temperatures,” *Bioresour. Technol.*, vol. 101, pp. 469–475, 210AD, doi: <https://doi.org/10.1016/j.biortech.2009.07.039>.
- [185] S. MeiMei and 2*, JIANG YongGuang¹ & SHI Liang¹, “Electromicrobiology and biotechnological applications of the exoelectrogens *Geobacter* and *Shewanella* spp.,” *Microbial Electrochemical Technology*, vol. 62, pp. 1670–1678, 2019, doi: <https://doi.org/10.1007/s11431-019-9509-8>.
- [186] T. Cai *et al.*, “Application of advanced anodes in microbial fuel cells for power generation: A review,” *Chemosphere*, vol. 248, p. 125985, Jun. 2020, doi: [10.1016/J.CHEMOSPHERE.2020.125985](https://doi.org/10.1016/J.CHEMOSPHERE.2020.125985).
- [187] R. Jinisha, J. Jerlin Regin, and J. Maheswaran, “A review on the emergence of single-chamber microbial fuel cell on wastewater treatment,” *IOP Conf Ser Mater Sci Eng*, vol. 983, no. 1, p. 012002, Nov. 2020, doi: [10.1088/1757-899X/983/1/012002](https://doi.org/10.1088/1757-899X/983/1/012002).
- [188] * Marco Zeppilli *et al.*, “Tetrachloroethane (TeCA) removal through sequential graphite-mixed metal oxide electrodes in a bioelectrochemical reactor,” *Environmental Science and Ecotechnology*, vol. Environment, 2023, doi: <http://dx.doi.org/10.1016/j.ese.2023.100309>.
- [189] R. Jenani, S. Karishmaa, A. Babu Ponnusami, P. Senthil Kumar, and G. Rangasamy, “A recent development of low-cost membranes for microbial fuel cell applications,” *Desalination Water Treat*, vol. 320, p. 100698, Oct. 2024, doi: [10.1016/J.DWT.2024.100698](https://doi.org/10.1016/J.DWT.2024.100698).
- [190] W. J. Keller KLRapp-Giles BJ, Semkiw ESPorat IBrown SD, “New Model for Electron Flow for Sulfate Reduction in *Desulfovibrio alaskensis* G20,” *Appl Environ Microbiol*, vol. 80, 2014, doi: <https://doi.org/10.1128/AEM.02963-13>.
- [191] N. N. Zheng X, “Cattle wastes as substrates for bioelectricity production via microbial fuel cells,” *Biotechnol Lett*, vol. 12, pp. 1809–14, 2010, doi: <https://doi.org/10.1007/s10529-010->

- [192] G. K. Oluwaseun Adelaja, Tajalli Keshavarz, "The effect of salinity, redox mediators and temperature on anaerobic biodegradation of petroleum hydrocarbons in microbial fuel cells," *Journal of Hazardous Materials*, vol. 283, pp. 211–217, 2015, doi: <https://doi.org/10.1016/j.jhazmat.2014.08.066>.
- [193] Y. M. Z.W. F. LiuF. X. Tan, L. H. Zhang, "Osmotic Pressure Compensated Solute Ectoine Improves Salt Tolerance of Microbial Cells in Microbial Fuel Cells," *Fuel Cells*, vol. 19, pp. 616–622, 2019, doi: <https://doi.org/10.1002/fuce.201900051>.
- [194] A.-R. C. Beecroft NJ, Zhao F, Varcoe JR, Slade RCT, Thumser AE, "Dynamic changes in the microbial community composition in microbial fuel cells fed with sucrose," *Appl Microbiol Biotechnol*, vol. 93, pp. 423–37, 2012, doi: <https://doi.org/10.1007/s00253-011-3590-y>.
- [195] M. S. Thulasinathan B, Jayabalan T, Sethupathi M, Kim W and et al Sengottuvelan N, "Bioelectricity generation by natural microflora of septic tank wastewater (STWW) and biodegradation of persistent petrogenic pollutants by basidiomycetes fungi: An integrated microbial fuel cell system.," *J Hazard Matererial*, vol. 412, p. 125228, 2021, doi: <https://doi.org/10.1016/j.jhazmat.2021.125228>.
- [196] J. T. Ramu SM, Thulasinathan B, Gujuluva Hari D, Bora A and et al Mohammed SN, "Fermentative hydrogen production and bioelectricity generation from food based industrial waste: An integrative approach," *Bioresour Technol*, vol. 310, p. 123447, 2020, doi: <https://doi.org/10.1016/j.biortech.2020.123447>.
- [197] J. T. Thulasinathan B, Ebenezer JO, Bora A, Nagarajan A, Pugazhendhi A and E. Al., "Bioelectricity generation and analysis of anode biofilm metabolites from septic tank wastewater in microbial fuel cells," *Int J Energy Res*, vol. 12, pp. 17244–58, 2021, doi: <https://doi.org/10.1002/er.5734>.
- [198] L. Wang, B. Xie, N. Gao, B. Min, and H. Liu, "Urea removal coupled with enhanced electricity generation in single-chambered microbial fuel cells," *Environmental Science and Pollution Research* 2017 24:25, vol. 24, no. 25, pp. 20401–20408, Jul. 2017, doi: [10.1007/S11356-017-9689-7](https://doi.org/10.1007/S11356-017-9689-7).
- [199] M. Zeppilli *et al.*, "Tetrachloroethane (TeCA) removal through sequential graphite-mixed metal oxide electrodes in a bioelectrochemical reactor," *Environmental Science and Ecotechnology*, vol. 17, p. 100309, Jan. 2024, doi: [10.1016/J.ESE.2023.100309](https://doi.org/10.1016/J.ESE.2023.100309).
- [200] L. B. Min B, Cheng S, "Electricity generation using membrane and salt bridge microbial fuelcells.," *Water Res*, vol. 39, pp. 1675–86, 2005, doi: <https://doi.org/10.1016/j.watres.2005.02.002>.
- [201] N. Mansoorian, H.J.; Mahvi, A.H.; Jafari, A.J.; Khanjani, "Evaluation of dairy industry wastewater treatment and simultaneous bioelectricity generation in a catalyst-less and mediator-less membrane microbial fuel cell," *J. Saudi Chem. Soc*, vol. 20, pp. 88–100, 2016.
- [202] et al Ryu JH, Lee HL, Lee YP, Kim TS, Kim MK, Anh DTN, "Simultaneous carbon and nitrogen removal from piggery wastewater using loop configuration," *Process Biochem*, vol. 48, pp. 1080–5, 2013, doi: <https://doi.org/10.1016/j.procbio.2013.05.016>.
- [203] et al. Thung W-E, Ong S-A, Ho L-N, Wong Y-S, Oon Y-L, Oon Y-S, "Simultaneous wastewater treatment and power generation with innovative design of an upflow membrane-less

- microbial fuel cell. Water, Air, Soil Pollut,” *Water Air Soil Pollut*, vol. 226, 2015, doi:<https://doi.org/10.1007/s11270-015-2410-x>.
- [204] van der D. K. Chin-A-Woeng TFC, Bloemberg GV, van der Bij AJ and et al. Schripsema J, KroonB, “Biocontrol by phenazine-1-carboxamide-producing *Pseudomonas chlororaphis* PCL1391 of tomato root rot caused by *Fusarium oxysporum* f. sp. *radicis-lycopersici*. Mol Plant-Microbe Interact,” *The American Phytopathological Society*, vol. 11, pp. 1069–77, 2007, doi: <https://doi.org/10.1094/MPMI.1998.11.11.1069>.
- [205] B. DR. Marsili E, Baron DB, Shikhare ID, Coursolle D, Gralnick JA, “Shewanella secretes flavins that mediate extracellular electron transfer,” *Proc Natl Acad Sci*, vol. 105, pp. 3968–73, 2008, doi: <https://doi.org/10.1073/pnas.0710525105>.
- [206] K. K. Masuda M, Freguia S, Wang Y-F, Tsujimura S, “Flavins contained in yeast extract are exploited for anodic electron transfer by *Lactococcus lactis*,” *Bioelectrochemistry*, vol. 78, pp. 173–5, 2010, doi: <https://doi.org/10.1016/j.bioelechem.2009.08.004>.
- [207] J. T. Thulasinathan B, Ebenezer JO, Bora A, Nagarajan A, Pugazhendhi A and E. Al., “Bioelectricity generation and analysis of anode biofilm metabolites from septic tank wastewater in microbial fuel cells,” *Int J Energy Res*, vol. 45, pp. 17244–77, 2021, doi: <https://doi.org/10.1002/er.5734>.
- [208] C. JM. Wu SJ, Hu ZH, Zhang LL, Yu X, “A novel dichloromethane-degrading *Lysinibacillus sphaericus* strain wh22 and its degradative plasmid,” *Appl Microbiol Biotechnol*, vol. 82, pp. 731–42, 2009, doi: <https://doi.org/10.1007/s00253-009-1873-3>.
- [209] F. A. Inglesby AE, Beatty DA, “Inglesby AE, Beatty DA, Fisher AC. Rhodospseudomonas palustris purple bacteria fed *Arthrospira maxima* cyanobacteria: Demonstration of application in microbial fuel cells,” *RSC Adv*, vol. 11, p. 4829, 2012, doi: <https://doi.org/10.1039/c2ra20264f>.
- [210] R. N. Feng Y, Yang Q, Wang X, Liu Y, Lee He, “Treatment of biodiesel production wastes with simultaneous electricity generation using a single-chamber microbial fuel cell,” *Bioresour Technol*, vol. 102, pp. 411–5, 2011, doi: <https://doi.org/10.1016/j.biortech.2010.05.059>.
- [211] B. et al Yu, J., Park, Y., Kim, “Power densities and microbial communities of brewery wastewater-fed microbial fuel cells according to the initial substrates,” *Bioprocess Biosyst Eng*, vol. 38, pp. 85–92, 2015, doi: <https://doi.org/10.1007/s00449-014-1246-x>.
- [212] V. R. Nimje *et al.*, “Comparative bioelectricity production from various wastewaters in microbial fuel cells using mixed cultures and a pure strain of *Shewanella oneidensis*,” *Bioresour Technol*, vol. 104, pp. 315–323, Jan. 2012, doi: 10.1016/J.BIORTECH.2011.09.129.
- [213] X. Chen *et al.*, “Process design and techno-economic analysis of fuel ethanol production from food waste by enzymatic hydrolysis and fermentation,” *Bioresour Technol*, vol. 363, p. 127882, Nov. 2022, doi: 10.1016/J.BIORTECH.2022.127882.
- [214] A. N. Ghadge and M. M. Ghangrekar, “Performance of low-cost scalable air–cathode microbial fuel cell made from clayware separator using multiple electrodes,” *Bioresour Technol*, vol. 182, pp. 373–377, Apr. 2015, doi: 10.1016/J.BIORTECH.2015.01.115.
- [215] D. A. Corona-Martínez, S. Y. Martínez-Amador, J. A. Rodríguez-De la Garza, E. I. Laredo-

- Alcalá, and P. Pérez-Rodríguez, "Recent Advances in Scaling up Bioelectrochemical Systems: A Review," *Biotech 2025, Vol. 14, Page 8*, vol. 14, no. 1, p. 8, Jan. 2025, doi: 10.3390/BIOTECH14010008.
- [216] S. Niju and K. Priyadharshini, "A review on microbial fuel cell technology for Brewery industry wastewater treatment—From fundamentals to pilot scale studies," *Wiley Online Library S Niju, K Priyadharshini Environmental Progress & Sustainable Energy, 2023* • *Wiley Online Library*, vol. 42, no. 6, Nov. 2023, doi: 10.1002/EP.14191.
- [217] S. M. Daud *et al.*, "A critical review of ceramic microbial fuel cell: Economics, long-term operation, scale-up, performances and challenges," *Fuel*, vol. 365, p. 131150, Jun. 2024, doi: 10.1016/J.FUEL.2024.131150.
- [218] S. Kondaveeti, J. Lee, R. Kakarla, H. S. Kim, and B. Min, "Low-cost separators for enhanced power production and field application of microbial fuel cells (MFCs)," *Electrochim Acta*, vol. 132, pp. 434–440, Jun. 2014, doi: 10.1016/J.ELECTACTA.2014.03.046.
- [219] M. Ghasemi *et al.*, "Simultaneous wastewater treatment and electricity generation by microbial fuel cell: Performance comparison and cost investigation of using Nafion 117 and SPEEK as separators," *Desalination*, vol. 325, pp. 1–6, Sep. 2013, doi: 10.1016/J.DESAL.2013.06.013.
- [220] I. Das, S. Das, R. Dixit, and & M. M. Ghangrekar, "Goethite supplemented natural clay ceramics as an alternative proton exchange membrane and its application in microbial fuel cell", doi: 10.1007/s11581-020-03472-1.
- [221] M. Sharma, P. P. Das, T. Sood, A. Chakraborty, and M. K. Purkait, "Ameliorated polyvinylidene fluoride-based proton exchange membrane impregnated with graphene oxide, and cellulose acetate obtained from sugarcane bagasse for application in microbial fuel cell," *J Environ Chem Eng*, vol. 9, no. 6, p. 106681, Dec. 2021, doi: 10.1016/J.JECE.2021.106681.
- [222] X. Tang, K. Guo, H. Li, Z. Du, and J. Tian, "Microfiltration membrane performance in two-chamber microbial fuel cells," *Biochem Eng J*, vol. 52, no. 2–3, pp. 194–198, Nov. 2010, doi: 10.1016/J.BEJ.2010.08.007.
- [223] G. Pasternak, J. Greenman, and I. Ieropoulos, "Comprehensive Study on Ceramic Membranes for Low-Cost Microbial Fuel Cells," *ChemSusChem*, vol. 9, no. 1, pp. 88–96, Jan. 2016, doi: 10.1002/CSSC.201501320
- [224] P. V. Moharir and A. R. Tembhurkar, "Comparative performance evaluation of novel polystyrene membrane with Ultrex as Proton Exchange Membranes in Microbial Fuel Cell for bioelectricity production from food waste," *Bioresour Technol*, vol. 266, pp. 291–296, Oct. 2018, doi: 10.1016/J.BIORTECH.2018.06.085.
- [225] G. Hernández-Flores, A. Andrio, V. Compañ, O. Solorza-Feria, and H. M. Poggi-Varaldo, "Synthesis and characterization of organic agar-based membranes for microbial fuel cells," *J Power Sources*, vol. 435, p. 226772, Sep. 2019, doi: 10.1016/J.JPOWSOUR.2019.226772.
- [226] B. Das, S. Singh, A. Reddy, C. Wang, and V. Katiyar, "ScienceDirect Crosslinked poly (vinyl alcohol) membrane as separator for domestic wastewater fed dual chambered microbial fuel cells," *Int J Hydrogen Energy*, 2020, doi: 10.1016/j.ijhydene.2020.11.213.
- [227] F. C. do Nascimento *et al.*, "Formulation and characterization of crosslinked polyvinyl alcohol (PVA) membranes: effects of the crosslinking agents," *Polymer Bulletin*, vol. 78, no. 2, pp. 917–929, Feb. 2021, doi: 10.1007/S00289-020-03142-2/FIGURES/7.

- [228] A. L. Ahmad, N. M. Yusuf, and B. S. Ooi, "Preparation and modification of poly (vinyl) alcoholmembrane: Effect of crosslinking time towards its morphology," *Desalination*, vol. 287, pp. 35–40, Feb. 2012, doi: 10.1016/J.DESAL.2011.12.003.
- [229] M. Sharma, P. P. Das, T. Sood, A. Chakraborty, and M. K. Purkait, "Ameliorated polyvinylidene fluoride-based proton exchange membrane impregnated with graphene oxide, and celluloseacetate obtained from sugarcane bagasse for application in microbial fuel cell," *J Environ Chem Eng*, vol. 9, no. 6, p. 106681, Dec. 2021, doi: 10.1016/J.JECE.2021.106681.
- [230] G. Palanisamy, H. Y. Jung, T. Sadhasivam, M. D. Kurkuri, S. C. Kim, and S. H. Roh, "A comprehensive review on microbial fuel cell technologies: Processes, utilization, and advanced developments in electrodes and membranes," *J Clean Prod*, vol. 221, pp. 598–621, 2019, doi: 10.1016/j.jclepro.2019.02.172.
- [231] Y. A. Indriyani, E. Rustami, I. Rusmana, S. Anwar, G. Djajakirana, and D. A. Santosa, "Bioelectricity production of microbial fuel cells (MFCs) and the simultaneous monitoring using developed multi-channels Arduino UNO-based data logging system," *J Appl Electrochem*, vol. 54, no. 3, pp. 503–518, Mar. 2024, doi: 10.1007/S10800-023-01989-7.
- [232] A. R. Caparanga, A. S. Balatbat, and L. Tayo, "Effects of heavy metals (Fe³⁺/Cr⁶⁺) on low-level energy generation in a microbial fuel cell," in *IOP Conference Series: Materials Science and Engineering*, Institute of Physics Publishing, Jun. 2017. doi: 10.1088/1757-899X/206/1/012031.
- [233] P. Choudhury *et al.*, "Performance improvement of microbial fuel cells for waste water treatment along with value addition: A review on past achievements and recent perspectives," *Renewable and Sustainable Energy Reviews*, vol. 79, pp. 372–389, Nov. 2017, doi: 10.1016/J.RSER.2017.05.098.
- [234] P. S. B. R. K. G. G. V. S. S. S. a. S. V. S., "Bioaugmentation of an electrochemically active strain to enhance the electron discharge of mixed culture: process evaluation through electro-kinetic analysis," *RSC Adv*, vol. 2, pp. 677–688, 2011, doi: <https://doi.org/10.1039/C1RA00540E>.
- [235] J. Yu *et al.*, "Biofilm metagenomic characteristics behind high coulombic efficiency for propanethiol deodorization in two-phase partitioning microbial fuel cell," *Water Res*, vol. 246, p. 120677, Nov. 2023, doi: 10.1016/J.WATRES.2023.120677.
- [236] P. Srinophakun, A. Thanapimmetha, S. Plangsri, S. Vetchayakunchai, and M. Saisriyoot, "Application of modified chitosan membrane for microbial fuel cell: Roles of proton carrier site and positive charge," *J Clean Prod*, vol. 142, pp. 1274–1282, Jan. 2017, doi: 10.1016/J.JCLEPRO.2016.06.153.
- [237] V. Aiswarya, S. Das, S. Kumar, and A. Datta, "Preparation and characterization of magnetized GO nanoparticle enhanced microencapsulated phase change material for thermal energy storage application," *Taylor & Francis V Aiswarya, S Das, S Kumar, A Datta Indian Chemical Engineer, 2022•Taylor & Francis*, vol. 64, no. 5, pp. 519–529, 2022, doi: 10.1080/00194506.2022.2066577.
- [238] M. Sharma, P. Mondal, A. D. Sontakke, A. Chakraborty, and M. K. Purkait, "High performance graphene-oxide doped cellulose acetate-based ion exchange membrane for environmental remediation applications," *Taylor & Francis M Sharma, P Mondal, AD Sontakke, A*

Chakraborty, MK Purkait *International Journal of Environmental Analytical Chemistry*, 2023•Taylor & Francis, vol. 103, no. 19, pp. 7751–7772, 2023, doi: 10.1080/03067319.2021.1975276.

- [239] Z. Zakaria, S. K. Kamarudin, S. N. Tumiat, and M. S. Masdar, “New composite membrane poly(vinyl alcohol)/graphene oxide for direct ethanol–proton exchange membrane fuel cell,” *J Appl Polym Sci*, vol. 136, no. 2, Jan. 2019, doi: 10.1002/APP.46928.
- [240] P. Srinophakun, A. Thanapimmetha, S. Plangsri, S. Vetchayakunchai, and M. Saisriyoot, “Application of modified chitosan membrane for microbial fuel cell: Roles of proton carrier site and positive charge,” *J Clean Prod*, vol. 142, pp. 1274–1282, Jan. 2017, doi: 10.1016/J.JCLEPRO.2016.06.153.
- [241] A. Roy *et al.*, “Per and Poly-Fluoroalkyl-Free PVA Membrane Separator for Sustainable Energy Recovery From Municipal Wastewater Using Biomimetic Miniature Microbial Fuel Cell,” *J Appl Polym Sci*, vol. 0, p. 57809, 2025, doi: 10.1002/APP.57809.
- [242] A. Montanari *et al.*, “‘Panta Rhei—everything flows’: change in hydrology and society—the IAHS scientific decade 2013–2022,” *Taylor & Francis A Montanari, G Young, HHG Savenije, D Hughes, T Wagener, LL Ren, D Kouts Yiannis, Hydrological Sciences Journal*, 2013 *Taylor & Francis*, vol. 58, no. 6, pp. 1256–1275, 2013, doi: 10.1080/02626667.2013.809088.
- [243] S. Sharma and S. Soederberg, “Review of International Political Economy Redesigning the business of development: the case of the World Economic Forum and global risk management,” 2019, doi: 10.1080/09692290.2019.1640125.
- [244] G. Halkos and E. C. Gkampoura, “Where do we stand on the 17 Sustainable Development Goals? An overview on progress,” *Econ Anal Policy*, vol. 70, pp. 94–122, Jun. 2021, doi: 10.1016/J.EAP.2021.02.001.
- [245] R. C. Buck *et al.*, “Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins,” *Integr Environ Assess Manag*, vol. 7, no. 4, pp. 513–541, Oct. 2011, doi: 10.1002/IEAM.258.
- [246] C. A. McDonough *et al.*, “Unsaturated PFOS and other PFASs in human serum and drinking water from an aff-impacted community,” *Environ Sci Technol*, vol. 55, no. 12, pp. 8139–8148, Jun. 2021, doi: 10.1021/ACS.EST.1C00522.
- [247] K. Li, P. Gao, P. Xiang, X. Zhang, X. Cui, and L. Q. Ma, “Molecular mechanisms of PFOA-induced toxicity in animals and humans: Implications for health risks,” *Environ Int*, vol. 99, pp. 43–54, 2017, doi: 10.1016/J.ENVINT.2016.11.014,
- [248] N. Boulif, R. Evers, M. Houben, Z. Borneman, and K. Nijmeijer, “Structure and performance of clay composite membranes with improved sodium conductivity for salinity gradient batteries,” *Appl Clay Sci*, vol. 245, p. 107136, Dec. 2023, doi: 10.1016/J.CLAY.2023.107136.
- [249] M. A. Rasool, C. Van Goethem, and I. F. J. Vankelecom, “Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes,” *Sep Purif Technol*, vol. 232, p. 115903, Feb. 2020, doi: 10.1016/J.SEPPUR.2019.115903.
- [250] D. Thiruselvi *et al.*, “A critical review on global trends in biogas scenario with its up-gradation techniques for fuel cell and future perspectives,” *Elsevier*, vol. 46, no. 31, pp. 16734–16750, May 2021, doi: 10.1016/J.IJHYDENE.2020.10.023.
- [251] A. Choudhury *et al.*, “Effect of electrode surface properties on enhanced electron transfer activity in microbial fuel cells,” *Eng Life Sci*, vol. 17, no. 2, pp. 186–192, Feb. 2017, doi:

10.1002/ELSC.201600063;

- [252] M. G. Waller and T. A. Trabold, "Review of Microbial Fuel Cells for Wastewater Treatment: Large-Scale Applications, Future Needs and Current Research Gaps," *ASME 2013 11th Int. Conf. on Fuel Cell Science, Eng. and Technology Collocated with the ASME 2013 Heat Transfer Summer Conf. and the ASME 2013 7th Int. Conf. on Energy Sustainability, FUELCELL 2013*, Dec.2013, doi: 10.1115/FUELCELL2013-18185.
- [253] N. J. Koffi and S. Okabe, "Domestic wastewater treatment and energy harvesting by serpentine up-flow MFCs equipped with PVDF-based activated carbon air-cathodes and a low voltage booster," *Chemical Engineering Journal*, vol. 380, p. 122443, Jan. 2020, doi: 10.1016/J.CEJ.2019.122443.
- [254] K. S. Aiyer, "How does electron transfer occur in microbial fuel cells" *World J Microbiol Biotechnol*, vol. 36, no. 2, pp. 1–9, Feb. 2020, doi: 10.1007/S11274-020-2801-Z
- [255] M. Rahimnejad, "MFCs' challenges and their potential solutions," *Biological Fuel Cells: Fundamental to Applications*, pp. 225–248, Jan. 2023, doi: 10.1016/B978-0-323-85711-6.00007-2.
- [256] H. Ren, C. Jiang, and J. Chae, "Effect of temperature on a miniaturized microbial fuel cell(MFC)," *Micro and Nano Systems Letters*, vol. 5, no. 1, pp. 1–7, Dec. 2017, doi: 10.1186/S40486-017-0048-8/TABLES/1.
- [257] H. Ren, H. S. Lee, and J. Chae, "Miniaturizing microbial fuel cells for potential portable powersources: promises and challenges," *Microfluid Nanofluid*, vol. 13, no. 3, pp. 353–381, Sep. 2012, doi: 10.1007/s10404-012-0986-7.
- [258] H. M. Poggi-Varaldo, J. E. Borbolla-Gaxiola, M. T. Ponce-Noyola, and O. Solorza-Feria, "Evaluation of a Low-Cost Device for Monitoring Potential and Enrichment of Microbial Cultures Used in a Biocathode Microbial Fuel Cell", Accessed: May 25, 2025.
- [259] R. Yousefi, M. M. Mardanpour, and S. Yaghmaei, "Fabrication of the macro and micro-scale microbial fuel cells to monitor oxalate biodegradation in human urine," *Sci Rep*, vol. 11, no. 1, p. 14346, Dec. 2021, doi: 10.1038/S41598-021-93844-Y.
- [260] H. Ren, C. I. Torres, P. Parameswaran, B. E. Rittmann, and J. Chae, "Improved current and power density with a micro-scale microbial fuel cell due to a small characteristic length," *Biosens Bioelectron*, vol. 61, pp. 587–592, Nov. 2014, doi: 10.1016/J.BIOS.2014.05.037.
- [261] M. Omenesa Idris, N. Asshifa Md Noh, M. Nasir Mohamad Ibrahim, and A. Ali Yaqoob, "Sustainable microbial fuel cell functionalized with a bio-waste: A feasible route to formaldehyde bioremediation along with bioelectricity generation," *Chemical Engineering Journal*, vol. 455, p. 140781, Jan. 2023, doi: 10.1016/J.CEJ.2022.140781.
- [262] N. Bazina, T. G. Ahmed, M. Almdaaf, S. Jibia, and M. Sarker, "Power generation from wastewater using microbial fuel cells: A review," *J Biotechnol*, vol. 374, pp. 17–30, Sep. 2023, doi: 10.1016/j.jbiotec.2023.07.006.
- [263] K. Elmaadawy *et al.*, "Microalgae-assisted fixed-film activated sludge MFC for landfill leachate treatment and energy recovery," *Process Safety and Environmental Protection*, vol. 160, pp. 221–231, Apr. 2022, doi: 10.1016/J.PSEP.2022.02.021.
- [264] B. R. Ringeisen *et al.*, "High power density from a miniature microbial fuel cell using

- Shewanella oneidensis DSP10,” *Environ Sci Technol*, vol. 40, no. 8, pp. 2629–2634, May 2006, doi: 10.1021/ES052254W.
- [265] M. Tesfaye, R. Patwa, P. Dhar, and V. Katiyar, “Nanosilk-grafted poly (lactic acid) films: Influence of cross-linking on rheology and thermal stability,” *ACS Omega*, vol. 2, no. 10, pp. 7071–7084, Oct. 2017, doi: 10.1021/ACSOMEGA.7B01005.
- [266] S. Choi, “Microscale microbial fuel cells: Advances and challenges,” *Biosens Bioelectron*, vol. 69, pp. 8–25, Jul. 2015, doi: 10.1016/J.BIOS.2015.02.021.
- [267] G. Chen, B. Wei, Y. Luo, B. E. Logan, and M. A. Hickner, “Polymer separators for high-power, high-efficiency microbial fuel cells,” *ACS Appl Mater Interfaces*, vol. 4, no. 12, pp. 6454–6457, Dec. 2012, doi: 10.1021/AM302301T/SUPPL_FILE/AM302301T_SI_001.PDF.
- [268] M. Brinc and A. Belič, “Optimization of process conditions for mammalian fed-batch cell culture in automated micro-bioreactor system using genetic algorithm,” *J Biotechnol*, vol. 300, pp. 40–47, Jul. 2019, doi: 10.1016/J.JBIOTEC.2019.05.001.
- [269] M. Tesfaye, R. Patwa, P. Dhar, and V. Katiyar, “Nanosilk-grafted poly (lactic acid) films: Influence of cross-linking on rheology and thermal stability,” *ACS Omega*, vol. 2, no. 10, pp. 7071–7084, Oct. 2017, doi: 10.1021/ACSOMEGA.7B01005,.
- [270] S. Choi, “Microscale microbial fuel cells: Advances and challenges,” *Biosens Bioelectron*, vol. 69, pp. 8–25, Jul. 2015, doi: 10.1016/j.bios.2015.02.021.
- [271] A. Sharma, L. Jelavic, and K. Herkendell, “Next-Generation Proton-Exchange Membranes in Microbial Fuel Cells: Overcoming Nafion’s Limitations,” *Energy Technology*, vol. 12, no. 6, p. 2301346, Jun. 2024, doi: 10.1002/ENTE.202301346.
- [272] V. Vatanpour, O. O. Teber, M. Mehrabi, and I. Koyuncu, “Polyvinyl alcohol-based separation membranes: a comprehensive review on fabrication techniques, applications and future prospective,” *Mater Today Chem*, vol. 28, p. 101381, Mar. 2023, doi: 10.1016/J.MTCHEM.2023.101381.
- [273] A. Roy, A. Kumar, A. Ebihara, C. T. Wang, and V. Katiyar, “A critical review on advancing bioinspired smart membranes for green energy recovery in microbial fuel cells: Paving the way for a sustainable future,” *J Environ Chem Eng*, vol. 13, no. 5, p. 118094, Oct. 2025, doi: 10.1016/J.JECE.2025.118094.
- [274] C. F. Kwiatkowski *et al.*, “Scientific Basis for Managing PFAS as a Chemical Class,” *Environ Sci Technol Lett*, vol. 7, no. 8, pp. 532–543, Aug. 2020, doi: 10.1021.
- [275] C. Y. Wong *et al.*, “Development of Poly (Vinyl Alcohol)-Based Polymers as Proton Exchange Membranes and Challenges in Fuel Cell Application: A Review,” *Polymer Reviews*, vol. 60, no. 1, pp. 171–202, Jan. 2020, doi: 10.1080/15583724.2019.1641514.
- [276] L. Kwiatkowski *et al.*, “Twenty-first-century ocean warming, acidification, deoxygenation, and upper-ocean nutrient and primary production decline from CMIP6 model projections,” *Biogeosciences*, vol. 17, no. 13, pp. 3439–3470, Jul. 2020, doi: 10.5194/BG-17-3439-2020.
- [277] L. Sun, J. Wang, J. Liang, and G. Li, “Boric Acid Cross-linked 3D Polyvinyl Alcohol Gel Beads by NaOH-Titration Method as a Suitable Biomass Immobilization Matrix,” *J Polym Environ*, vol. 28, no. 2, pp. 532–541, Feb. 2020, doi: 10.1007/S10924-019-01610-Z/FIGURES/6.
- [278] S. Mondal, F. Papiya, S. N. Ash, and P. P. Kundu, “Composite membrane of sulfonated polybenzimidazole and sulfonated graphene oxide for potential application in microbial fuel

- cell,” *J Environ Chem Eng*, vol. 9, no. 1, p. 104945, Feb. 2021, doi: 10.1016/J.JECE.2020.104945.
- [279] K. C. S. Figueiredo, T. L. M. Alves, and C. P. Borges, “Poly(vinyl alcohol) films crosslinked by glutaraldehyde under mild conditions,” *J Appl Polym Sci*, vol. 111, no. 6, pp. 3074–3080, Jan. 2009, doi: 10.1002/APP.29263.
- [280] Y. Dai *et al.*, “Enhanced mechanical, thermal, and UV-shielding properties of poly (vinyl alcohol)/metal–organic framework nanocomposites,” *RSC Adv*, vol. 8, no. 67, pp. 38681–38688, Nov. 2018, doi: 10.1039/C8RA07143H.
- [281] S. S. Gaur, P. Dhar, A. Sonowal, A. Sharma, A. Kumar, and V. Katiyar, “Thermo-mechanically stable sustainable polymer-based solid electrolyte membranes for direct methanol fuel cell applications,” *J Memb Sci*, vol. 526, pp. 348–354, Mar. 2017, doi: 10.1016/J.MEMSCI.2016.12.030.
- [282] R. Hu, J. Zhao, Y. Wang, Z. Li, and J. Zheng, “A highly stretchable, self-healing, recyclable and interfacial adhesion gel: Preparation, characterization and applications,” *Chemical Engineering Journal*, vol. 360, pp. 334–341, Mar. 2019, doi: 10.1016/J.CEJ.2018.12.001.
- [283] C. Yang, Z.; Pei, H.; Hou, Q.; Jiang, L.; Zhang, L.; Nie, “Algal biofilm-assisted microbial fuel cell to enhance domestic wastewater treatment: Nutrient, organics removal and bioenergy production,” *Chem. Eng. J*, vol. 332, pp. 277–285, 2018.
- [284] Y. Hindatu, M. S. M. Annuar, and A. M. Gumel, “Mini-review: Anode modification for improved performance of microbial fuel cell,” *Renewable and Sustainable Energy Reviews*, vol. 73, no. January, pp. 236–248, 2017, doi: 10.1016/j.rser.2017.01.138.
- [285] A. M. et Al, “Effective power management system in stacked microbial fuel cells for onsite applications,” *J Power Sources*, vol. 517, 2022, doi: <https://doi.org/10.1016/j.jpowsour.2021.230684>.
- [286] Bhanupriya Das Surendra Singh Gaur Anki Reddy Katha Chin Tsan Wang Vimal Katiyar, “Hair hydrolysate functionalized cellulose nanocrystal-based chitosan membrane to harness power from wastewater fed MFCs,” *Int J Hydrogen Energy*, vol. 48, pp. 9451–9461, 2023, doi: <https://doi.org/10.1016/j.ijhydene.2022.12.054>.
- [287] R. E. A. M. F.S. Fadzli, S.A. Bhawani, “Microbial fuel cell: recent developments in organics substrate use and bacterial electrode interaction,” *J. Chem.*, vol. 2021, p. 16, 2021, doi: <https://doi.org/10.1155/2021/4570388>.
- [288] H. F. Y. Ma, M. Rajkumar, Y. Luo, “Inoculation of endophytic bacteria on host and non-host plants—effects on plant growth and Ni uptake,” *J. Hazard Mater.*, vol. 195, pp. 230–237, 2011, doi: <https://doi.org/10.1016/j.jhazmat.2011.08.034>.
- [289] K. B. L. and L. L. Mu Chiao1, “Micromachined microbial and photosynthetic fuel cells,” <https://iopscience.iop.org/journal/0960-1317>.
- [290] et al Rezaei, Farzaneh, “Substrate-enhanced microbial fuel cells for improved remote power generation from sediment-based systems,” *Environ Sci Technol*, vol. 41, pp. 4053–4058, 2007, doi: <https://dx.doi.org/10.1021/es070426e>.
- [291] F. I. G. Di Lorenzo, “Regulatory events controlling ER-Phagy,” *Curr Opin Cell Biol*, vol. 76, 2022.
- [292] H. Lee, W. Yang, X. Wei, A. Fraiwan, and S. Choi, “A micro-sized microbial fuel cell-based biosensor for fast and sensitive detection of toxic substances in water,” in *Proceedings of the*

- IEEE International Conference on Micro Electro Mechanical Systems (MEMS)*, Institute of Electrical and Electronics Engineers Inc., Feb. 2015, pp. 573–576. doi: 10.1109/MEMSYS.2015.7051020.
- [293] M. et. al Tavakolian, “New design of benthic microbial fuel cell for bioelectricity generation: Comparative study,” *Int J Hydrogen Energy*, vol. 45, 2020, doi: <https://doi.org/10.1016/j.ijhydene.2020.06.181>.
- [294] M. et al. Chiao, “Micromachined microbial and photosynthetic fuel cells,” *J. Micromech cells Microeng*, vol. 16, pp. 2547–2553, 2006.
- [295] J. R. K. et Al, “Evaluation of procedures to acclimate a microbial fuel cell for electricity production,” *Appl Microbiol Biotechnol*, vol. 68, 2005, doi: 10.1007/s00253-004-1845-6.
- [296] shog I. E. P. A. Higa, “structural optimization of contact electrodes in microbial fuel cells for current density enhancement,” *sensors and actuators*, vol. 177, pp. 30–36, 2012.
- [297] Dr R. P. P. Ismail, M. Ali, “A PDMS Fabricated Miniature Microbial Fuel Cell,” *International Journal of Scientific & Technology Research*, vol. 3, 2014, doi: <https://www.ijstr.org/paper-references.php?ref=IJSTR-1014-10197>.
- [298] A. C. B. Arvind Kumar Ray M. Sindhuja S. Harinipriya, “Environmentally available biowastes as substrate in microbial fuel cell for efficient chromium reduction,” *Journal of Hazardous Materials*, vol. 355, pp. 197–205, 2018, doi: <https://doi.org/10.1016/j.jhazmat.2018.05.030>.
- [299] H. C. Tao, M. Liang, W. Li, L. J. Zhang, J. R. Ni, and W. M. Wu, “Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell,” *J Hazard Mater*, vol. 189, no. 1–2, pp. 186–192, May 2011, doi: 10.1016/J.JHAZMAT.2011.02.018.
- [300] M. Li *et al.*, “Simultaneous Cr(VI) reduction and bioelectricity generation in a dual chamber microbial fuel cell,” *Chemical Engineering Journal*, vol. 334, pp. 1621–1629, Feb. 2018, doi: 10.1016/J.CEJ.2017.11.144.
- [301] C. Abourached, T. Catal, and H. Liu, “Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production,” *Water Res*, vol. 51, pp. 228–233, Mar. 2014, doi: 10.1016/J.WATRES.2013.10.062.
- [302] Z. Wang, B. Lim, and C. Choi, “Removal of Hg²⁺ as an electron acceptor coupled with power generation using a microbial fuel cell,” *Bioresour Technol*, vol. 102, no. 10, pp. 6304–6307, May 2011, doi: 10.1016/J.BIORTECH.2011.02.027.
- [303] C. Choi and Y. Cui, “Recovery of silver from wastewater coupled with power generation using a microbial fuel cell,” *Bioresour Technol*, vol. 107, pp. 522–525, Mar. 2012, doi: 10.1016/J.BIORTECH.2011.12.058.
- [304] C. Choi and N. Hu, “The modelling of gold recovery from tetrachlorocuprate wastewater using a microbial fuel cell,” *Bioresour Technol*, vol. 133, pp. 589–598, Apr. 2013, doi: 10.1016/J.BIORTECH.2013.01.143.
- [305] T. ; M. Seidel, M.; Kugaraj, M.; Nikolowski, K.; Wolter, M.; Kinski, I.; Jähnert, “Comparison of Electrochemical Degradation for Spray Dried and Pulse Gas Dried LiNi_{0.5}Mn_{1.5}O₄,” *J. Electrochem. Soc*, vol. 166, pp. A2860–A2869, 2019.
- [306] K. Vimal and R. B. V. Appa, “Chemically modified biopolymer as an eco-friendly corrosion

- inhibitor for mild steel in a neutral chloride environment,” *New Journal of Chemistry*, vol. 41, no. 14, pp. 6278–6289, 2017, doi: 10.1039/c7nj00553a.
- [307] Y. Gençten, M.; Dönmez, K.; , Sahin, “Investigation of the Temperature Effect on Electrochemical Behaviours of TiO₂ for Gel Type Valve Regulated Lead-Acid Batteries,” *A Appl.Sci. Eng*, vol. 17, p. 882, 2016.
- [308] K. Chun Yik Wong, Wai Yin Wong, Kee Shyuan Loh, Wan Ramli Wan Daud and M. K. & R. W.Long Lim, “Development of Poly(Vinyl Alcohol)-Based Polymers as Proton Exchange Membranes and Challenges in Fuel Cell Application: A Review,” *Polymer Review*, 2019, .
- [309] G. M. Ghadge AN, “Development of low-cost ceramic separator using mineral cation exchanger to enhance the performance of microbial fuel cells.,” *Electrochimacta*, vol. 166, pp. 320–8, 2015, doi: <https://doi.org/10.1016/j.electacta.2015.03.105>.
- [310] A. J. Philips J, Verbeeck K, Rabaey K, “Electron transfer mechanisms in biofilms.,” *Microbialelectrochemical fuel cells fundamentals applications*, pp. 67–113, 2016, doi: <https://doi.org/10.1016/B978-1-78242-375-1.00003-4>.
- [311] Hui Wang Xizi Long Yingying Sun, D. Wang, and et.al, “Electrochemical impedance spectroscopy applied to microbial fuel cells: A review,” *Front. Microbiol.*, vol. 13, 2022, doi:<https://doi.org/10.3389/fmicb.2022.973501>.
- [312] and J. M. G. Watkins, Nicholas B. Zachary J. Schiffer, Yungchieh Lai, Charles B. Musgrave III, Harry A. Atwater, William A. Goddard III, Theodor Agapie*, Jonas C. Peters*, “Hydrodynamics Change Tafel Slopes in Electrochemical CO₂ Reduction on Copper,” *ACS Energy Lett.*, vol. 8, pp.2185–2192, 2023, doi: <https://doi.org/10.1021/acsenenergylett.3c00442>.
- [313] D. Yu, L. Bai, J. Zhai, Y. Wang, and S. Dong, “Toxicity detection in water containing heavy metalions with a self-powered microbial fuel cell-based biosensor,” *Talanta*, vol. 168, pp. 210–216,Jun. 2017, doi: 10.1016/j.talanta.2017.03.048.
- [314] M. C. Neil V. Rees Richard G. Compton Henstridge, “A comparison of the Butler–Volmer and asymmetric Marcus–Hush models of electrode kinetics at the channel electrode,” *J of the Electroanalytical chemistry*, vol. 687, pp. 79–83, 2012
- [315] G. MM. [35] Neethu B, Bhowmick GD, “A novel proton exchange membrane developed from carbon derived from coconut shell for application in a microbial fuel cell,” *Biochem Eng J*, vol.7, pp. 148–170, 2019, doi: <https://doi.org/10.1016/j.bej.2019.05.011>.
- [316] F. Y.Z. and E. Al., “Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration.,” *J. Power Sources*, vol. 171, pp. 348–354, 2007,doi: <https://doi.org/10.1016/j.jpowsour.2007.06.220>.
- [317] B. R. et al. Ringeisen, “High power density from a miniature microbial fuel cell using *Shewanella oneidensis* DSP10,” *Environ Sci Technol*, vol. 40, pp. 2629–2634, 2006.
- [318] H. et al. Hou, “Microfabricated microbial fuel cell arrays reveal electrochemically active microbes.,” *PLoS ONE*, 2004.
- [319] J. C. et al. Biffinger, “Characterization of electrochemically active bacteria utilizing a high-throughput voltage-based screening assay.,” *Biotechnol. Bioeng.*, vol. 102, pp. 436–444, 2009, doi: <https://doi.org/10.1002/bit.22072>.
- [320] Et. al Nikhil S. Mavlankar, Joanne Lau, Kelly P. Nevin. Ashley E. Franks, “Electrical

- Conductivity in a Mixed-Species Biofilm,” *Appl Environ Microbiol*, vol. 78, pp. 5967–5971, 2012, doi: <https://doi.org/10.1128%2FAEM.01803-12>.
- [321] Et. al Abhijeet P. Borole, Gemma Reguera, Bradley Ringeisen, “Electroactive biofilms: Current status and future research needs,” *Science, Energy and Environmental*, vol. 4, pp. 4813–4834, 2011, doi: <https://doi.org/10.1039/C1EE02511B>.
- [322] S. Dhara, N. Shekhar Samanta, P. P. Das, R. V. S. Uppaluri, and M. K. Purkait, “Ravenna Grass-Extracted Alkaline Lignin-Based Polysulfone Mixed Matrix Membrane (MMM) for Aqueous Cr(VI) Removal,” *ACS Appl Polym Mater*, vol. 5, no. 8, pp. 6399–6411, Aug. 2023.
- [323] B. Das *et al.*, “Low-cost crosslinked PVA membranes as alternative proton exchange membrane in hemodialysis wastewater fed bioelectrochemical fuel cells,” *Process Safety and Environmental Protection*, vol. 196, p. 106915, Apr. 2025, doi: 10.1016/J.PSEP.2025.106915.
- [324] “Home | Ministry of Labour & Employment | GoI|India.” Jun. 08, 2025. <https://labour.gov.in/>
- [325] S. M. Safwat, A. Khaled, A. Elawwad, and M. E. Matta, “Dual-chamber microbial fuel cells as biosensors for the toxicity detection of benzene, phenol, chromium, and copper in wastewater: Applicability investigation, effect of various catholyte solutions, and life cycle assessment,” *Process Safety and Environmental Protection*, vol. 170, pp. 1121–1136, Feb. 2023, doi: 10.1016/J.PSEP.2022.12.088.
- [326] E. Nasri *et al.*, “Cytotoxic effects of seven Tunisian hospital wastewaters on the proliferation of human breast cancer cell line MDA-231: correlation with their chemical characterization,” *Environmental Science and Pollution Research*, vol. 24, no. 25, pp. 20422–20428, Sep. 2017, doi: 10.1007/S11356-017-9717-7.
- [327] T. S. Oliveira, M. Al Aukidy, and P. Verlicchi, “Occurrence of Common Pollutants and Pharmaceuticals in Hospital Effluents,” *Handbook of Environmental Chemistry*, vol. 60, pp. 17–32, 2017, doi: 10.1007/698_2017_9.
- [328] M. Custodio, W. Cuadrado-Campó, R. Peñaloza, C. Vicuña-Orihuela, E. Torres-Gutiérrez, and E. Orellana, “Treatment of Hospital Wastewater Using Activated Sludge with Extended Aeration,” *Journal of Ecological Engineering*, vol. 23, no. 11, pp. 24–32, 2022, doi: 10.12911/22998993/152991.
- [329] P. Daraei *et al.*, “Novel thin film composite membrane fabricated by mixed matrix nanoclay/chitosan on PVDF microfiltration support: Preparation, characterization and performance in dye removal,” *J Memb Sci*, vol. 436, pp. 97–108, Jun. 2013, doi: 10.1016/J.MEMSCI.2013.02.031.
- [330] L. Qi, S. Li, L. Duan, S. W. Hermanowicz, and H. Y. Ng, “A review on membrane modification techniques for membrane fouling control: Mechanisms and membrane preparation,” *Crit Rev Environ Sci Technol*, vol. 55, no. 18, pp. 1455–1478, 2025, doi: 10.1080/10643389.2025.2543797.
- [331] S. Li, H. Zhang, Q. Gao, and L. Duan, “Formation of membrane fouling and removal mechanism of contaminants in osmotic microbial fuel cells in the presence of perfluoroalkyl substances,” *Water Res*, vol. 284, p. 124033, Sep. 2025, doi: 10.1016/J.WATRES.2025.124033.
- [332] S. Li, L. Duan, Q. Gao, and H. Zhang, “Performance impacts and removal potential of per- and poly-fluoroalkyl substances in osmotic microbial fuel cell,” *Sep Purif Technol*, vol. 357, p. 130236, May 2025, doi: 10.1016/J.SEPPUR.2024.130236.

- [333] K. P. Katuri and K. Scott, "Electricity generation from the treatment of wastewater with a hybrid up-flow microbial fuel cell," *Biotechnol Bioeng*, vol. 107, no. 1, pp. 52–58, Sep. 2010, doi: 10.1002/BIT.22778.
- [334] M. Hassan, S. Kanwal, R. S. Singh, M. Ali SA, M. Anwar, and C. Zhao, "Current challenges and future perspectives associated with configuration of microbial fuel cell for simultaneous energy generation and wastewater treatment," *Int J Hydrogen Energy*, vol. 50, pp. 323–350, Jan. 2024, doi: 10.1016/J.IJHYDENE.2023.08.134.
- [335] K. Elmaadawy *et al.*, "Microalgae-assisted fixed-film activated sludge MFC for landfill leachate treatment and energy recovery," *Process Safety and Environmental Protection*, vol. 160, pp. 221–231, Apr. 2022, doi: 10.1016/J.PSEP.2022.02.021.
- [336] A. Nawaz *et al.*, "Microbial fuel cells: Insight into simultaneous wastewater treatment and bioelectricity generation," *Process Safety and Environmental Protection*, vol. 161, pp. 357–373, May 2022, doi: 10.1016/J.PSEP.2022.03.039.
- [337] S. Kumar, M. Sharma, J. Thomas, C. T. Chang, and M. K. Purkait, "Faradic charged modified wrinkled layered graphene oxide as a capacitive deionization electrode for brackish water desalination," *Electrochim Acta*, vol. 538, Oct. 2025, doi: 10.1016/j.electacta.2025.146831.
- [338] F. Tarrass, M. Benjelloun, and O. Benjelloun, "Recycling Wastewater After Haemodialysis: An Environmental Analysis for Alternative Water Sources in Arid Regions," *American Journal of Kidney Diseases*, vol. 52, no. 1, pp. 154–158, Jul. 2008, doi: 10.1053/J.AJKD.2008.03.022.
- [339] F. Tarrass, M. Benjelloun, and G. B. Piccoli, "Haemodialysis water reuse within a circular economy approach. What can we add to current knowledge? A point of view," *J Nephrol*, vol. 37, no. 7, pp. 1801–1805, Sep. 2024, doi: 10.1007/S40620-024-01989-6/FIGURES/3.
- [340] P. J. Sarma and K. Mohanty, "Development and comprehensive characterization of low-cost hybrid clay-based ceramic membrane for power enhancement in plant based microbial fuel cells (PMFCs)," *Mater Chem Phys*, vol. 296, p. 127337, Feb. 2023, doi: 10.1016/J.MATCHEMPHYS.2023.127337.
- [341] M. A. Abu-Saied, E. A. Soliman, K. M. Abualnaj, and E. El Desouky, "Highly Conductive Polyelectrolyte Membranes Poly(vinyl alcohol)/Poly(2-acrylamido-2-methyl propane sulfonic acid) (PVA/PAMPS) for Fuel Cell Application," *Polymers 2021, Vol. 13, Page 2638*, vol. 13, no. 16, p. 2638, Aug. 2021, doi: 10.3390/POLYM13162638.
- [342] A. Sharma, L. Đeleović, and K. Herkendell, "Next-Generation Proton-Exchange Membranes in Microbial Fuel Cells: Overcoming Nafion's Limitations," *Energy Technology*, vol. 12, no. 6, p. 2301346, Jun. 2024.
- [343] S. Wang *et al.*, "High-strength hydrophilic N-halamines chitosan and cellulose nanofibers membranes with repeated bactericidal properties," *Int J Biol Macromol*, vol. 253, p. 127065, Dec. 2023, doi: 10.1016/J.IJBIOMAC.2023.127065.
- [344] K. Sharma *et al.*, "Cellulose-based membranes, hydrogels and aerogels for water treatment application," *Ind Crops Prod*, vol. 225, p. 120474, Mar. 2025, doi: 10.1016/J.INDCROP.2025.120474.
- [345] X. Miao, J. Lin, and F. Bian, "Utilization of discarded crop straw to produce cellulose nanofibrils and their assemblies," *Journal of Bioresources and Bioproducts*, vol. 5, no. 1, pp.

26–36, Feb. 2020, doi: 10.1016/J.JOBAB.2020.03.003.

- [346] D. Nikolaeva, K. Verachtert, I. Azcune, J. C. Jansen, and I. F. J. Vankelecom, “Influence of ionic liquid-like cationic pendants composition in cellulose-based polyelectrolytes on membrane-based CO₂ separation,” *Carbohydr Polym*, vol. 255, p. 117375, Mar. 2021, doi: 10.1016/J.CARBPOL.2020.117375.
- [347] A. Ahmad *et al.*, “Self-sterilised composite membranes of cellulose acetate/polyethene glycol for water desalination,” *Carbohydr Polym*, vol. 149, pp. 207–216, Sep. 2016, doi: 10.1016/J.CARBPOL.2016.04.104.
- [348] R. Haddad, E. Ferjani, M. S. Roudesli, and A. Deratani, “Properties of cellulose acetate nanofiltration membranes. Application to brackish water desalination,” *Desalination*, vol. 167, no. 1–3, pp. 403–409, Aug. 2004, doi: 10.1016/J.DESAL.2004.06.154.
- [349] F. Xiang *et al.*, “Advances of blend films based on natural food soft matter: Multi-scale structural analysis,” *Int J Biol Macromol*, vol. 258, p. 128770, Feb. 2024, doi: 10.1016/J.IJBIOMAC.2023.128770.
- [350] S. B. Aziz *et al.*, “Impedance, FTIR and transport properties of plasticized proton conducting biopolymer electrolyte based on chitosan for electrochemical device application,” *Results Phys*, vol. 29, p. 104770, Oct. 2021, doi: 10.1016/J.RINP.2021.104770.
- [351] S. W. K. H.J. Lee, Y. Cho, “Development of low-cost process for pore generation in cellulose acetate by utilising calcium salts,” *Journal of Industrial and Engineering Chemistry*, vol. 94, pp. 419–424, 21AD, doi: <https://doi.org/10.1016/j.jiec.2020.11.014>.
- [352] P. Ravikumar, S. S.- Polimery, and undefined 2021, “Influence of the addition of chitin nanocrystals on the characteristics of cellulose acetate films,” *ichp.vot. plP Ravikumar, S Sagadevan Polimery, 2021•ichp.vot.pl*, vol. 66, no. 2, 2021, doi: 10.14314/polimery.2021.2.2.
- [353] R. K. Saini, M. Rani, and U. Shanker, “Green biosynthesised N-doped nickel ferrite chitosan-coated nanocomposite for high photocatalytic degradation of organic pollutants from wastewater,” *Int J Biol Macromol*, vol. 306, p. 141446, May 2025, doi: 10.1016/J.IJBIOMAC.2025.141446.
- [354] X. Zhang, Z. Zhang, W. Wu, J. Yang, and Q. Yang, “Preparation and characterization of chitosan/Nano-ZnO composite film with antimicrobial activity,” *Bioprocess Biosyst Eng*, vol. 44, no. 6, pp. 1193–1199, Jun. 2021, doi: 10.1007/S00449-021-02521-X/FIGURES/7.
- [355] M. M. Armendáriz-Ontiveros *et al.*, “Modification of Thin Film Composite Membrane by Chitosan–Silver Particles to Improve Desalination and Anti-Biofouling Performance,” *Membranes 2022, Vol. 12, Page 851*, vol. 12, no. 9, p. 851, Aug. 2022, doi: 10.3390/MEMBRANES12090851.
- [356] N. Zhang, C. Gao, L. Meng, and X. Tang, “Preparation and characterization of carnauba wax-based particle with hierarchical structure and its use as hydrophobic coating for chitosan films,” *Carbohydr Polym*, vol. 319, p. 121224, Nov. 2023, doi: 10.1016/J.CARBPOL.2023.121224.
- [357] Y. Xu *et al.*, “Fabrication and Functional Regulation of Biomimetic Interfaces and Their Antifouling and Antibacterial Applications: A Review,” *Small*, vol. 20, no. 21, p. 2308091, May 2024.

- [358] A. Kramar, I. Rodríguez Ortega, G. González-Gaitano, and J. González-Benito, "Solution casting of cellulose acetate films: influence of surface substrate and humidity on wettability, morphology and optical properties," *Cellulose*, vol. 30, no. 4, pp. 2037–2052, Mar. 2023, doi: 10.1007/S10570-022-05026-2/FIGURES/9.
- [359] N. Liu, S. Bi, Y. Ou, H. Liu, Y. Zhang, and C. Gong, "Zwitterion-functionalized nanofiber-based composite proton exchange membranes with superior ionic conductivity and chemical stability for direct methanol fuel cells," *J Colloid Interface Sci*, vol. 674, pp. 925–937, Nov. 2024, doi: 10.1016/J.JCIS.2024.06.229.
- [360] X. Du, S. A. Rashid, L. C. Abdullah, and N. A. Rahman, "Preparation of electrospun cellulose acetate/chitosan membranes for efficient sorption of heavy metals from aqueous solutions," *Colloids Surf A Physicochem Eng Asp*, vol. 699, p. 134698, Oct. 2024, doi: 10.1016/J.COLSURFA.2024.134698.
- [361] H. Ahangari, A. Ebrahimi, A. Ehsani, and S. Amjadi, "Multipurpose packaging system based on intelligent carboxymethyl cellulose film and activated cellulose acetate electrospun nanofibers for seafoods," *Int J Biol Macromol*, vol. 298, p. 140115, Apr. 2025, doi: 10.1016/J.IJBIOMAC.2025.140115.
- [362] R. R. M. de Freitas, A. M. Senna, and V. R. Botaro, "Influence of degree of substitution on thermal dynamic mechanical and physicochemical properties of cellulose acetate," *Ind Crops Prod*, vol. 109, pp. 452–458, Dec. 2017, doi: 10.1016/J.INDCROP.2017.08.062.
- [363] R. Erdmann, S. Kabasci, and H. P. Heim, "Thermal Properties of Plasticized Cellulose Acetate and Its β -Relaxation Phenomenon," *Polymers 2021, Vol. 13, Page 1356*, vol. 13, no. 9, p. 1356, Apr. 2021, doi: 10.3390/POLYM13091356.
- [364] Z. M. Z. K. Chen, J. L. Yu, J. W. Huang, Q. Tang, H. P. Li, "Improved mechanical, water vapor barrier and UV-shielding properties of cellulose acetate films with flower-like metal-organic framework nanoparticles," *Int J Biol Macromol*, vol. 167, pp. 1–9, 2021.
- [365] X. L. G. X. J. Wang, X. L. Ba, N. Cui, Z. Ma, L. G. Wang, Z. P. Wang, "Preparation, characterisation, and desalination performance study of cellulose acetate membranes with MIL-53(Fe) additive," *J Memb Sci*, vol. 590, p. 9, 2019.
- [366] A. Aly, M. A. -I. journal of pharmaceuticals, and undefined 2021, "Nanofibers of cellulose acetate containing ZnO nanoparticles/graphene oxide for wound healing applications," *Elsevier AA Aly, MK Ahmed International journal of pharmaceuticals*, 2021[370] M. A. Vandiver *et al.*, "Mechanical Characterization of Anion Exchange Membranes by Extensional Rheology under Controlled Hydration," *J Electrochem Soc*, vol. 161, no. 10, pp. H677–H683, Jul. 2014, doi: 10.1149/2.0971410JES/XML.
- [371] S. Srivastava, "Investigation of mechanical and water absorption characterization of chitosan and rice bran reinforced biochar-based composites," *Iranian Polymer Journal (English Edition)*, vol. 34, no. 7, pp. 1029–1038, Jul. 2025, doi: 10.1007/S13726-024-01431-5.
- [372] J. Peng *et al.*, "Constructing novel cross-linked polybenzimidazole network for high-performance high-temperature proton exchange membrane," *Elsevier J Peng, X Fu, J Luo, Y Liu, L Wang, X Peng Journal of Membrane Science*, 2022
- [373] R. Castro-Muñoz, G. B.-C. O. in C. Engineering, and undefined 2025, "Paving the way for green cross-linker substances for the fabrication of polymer membranes—a review," *Elsevier*, Accessed: Jul. 02, 2025.

- [374] Y. Hamed, K. Hassan, H. Ahsan, M. H.-F. Chemistry, and undefined 2024, "Development of chitosan-based edible film incorporated with purified flavonoids from *Moringa oleifera*: Structural, thermal, antibacterial activity and," *Elsevier* YS Hamed, KR Hassan, HM Ahsan, M Hussain, J Wang, XG Zou, T Bu, AM Rayan, K Yang *Food Chemistry*.
- [375] O. O. Kolajo *et al.*, "Impact of cathode biofouling in microbial fuel cells and mitigation techniques," *Biocatal Agric Biotechnol*, vol. 43, p. 102408, Aug. 2022, doi: 10.1016/J.BCAB.2022.102408.
- [376] H. Yilmaz Atay, "Antibacterial Activity of Chitosan-Based Systems," *Functional Chitosan*, p. 457, Jan. 2020, doi: 10.1007/978-981-15-0263-7_15.
- [377] P. Srinophakun, A. Thanapimmetha, S. Plangsri, S. Vetchayakunchai, and M. Saisriyoot, "Application of modified chitosan membrane for microbial fuel cell: Roles of proton carrier site and positive charge," *J Clean Prod*, vol. 142, pp. 1274–1282, Jan. 2017, doi: 10.1016/J.JCLEPRO.2016.06.153.
- [378] V. Vatanpour *et al.*, "Cellulose acetate in fabrication of polymeric membranes: A review," *Chemosphere*, vol. 295, p. 133914, May 2022, doi: 10.1016/J.CHEMOSPHERE.2022.133914.
- [379] C. Liu and R. Bai, "Preparation of chitosan/cellulose acetate blend hollow fibers for adsorptive performance," *J Memb Sci*, vol. 267, no. 1–2, pp. 68–77, Dec. 2005, doi: 10.1016/J.MEMSCI.2005.06.001.
- [380] Q. Cheng *et al.*, "High specific surface crown ether modified chitosan nanofiber membrane by low-temperature phase separation for efficient selective adsorption of lithium," *Sep Purif Technol*, vol. 262, p. 118312, May 2021, doi: 10.1016/J.SEPPUR.2021.118312.
- [381] N. A. Bahmid *et al.*, "Cellulose acetate/chitosan composite film loaded with ground cinnamon for active packaging: water vapor sorption kinetic, compounds release, and antimicrobial effect," *Food Packag Shelf Life*, vol. 43, p. 101311, Jun. 2024, doi: 10.1016/J.FPSL.2024.101311.
- [382] J. Zhao, H. Liu, P. Xue, S. Tian, S. Sun, and X. Lv, "Highly-efficient PVDF adsorptive membrane filtration based on chitosan@CNTs-COOH simultaneous removal of anionic and cationic dyes," *Carbohydr Polym*, vol. 274, p. 118664, Nov. 2021, doi: 10.1016/J.CARBPOL.2021.118664.
- [383] M. J. Saadh *et al.*, "Advances in chitosan-based blends as potential drug delivery systems: A review," *Int J Biol Macromol*, vol. 273, p. 132916, Jul. 2024, doi: 10.1016/J.IJBIOMAC.2024.132916.
- [384] A. G. Boricha and Z. V. P. Murthy, "Preparation of N,O-carboxymethyl chitosan/cellulose acetate blend nanofiltration membrane and testing its performance in treating industrial wastewater," *Chemical Engineering Journal*, vol. 157, no. 2–3, pp. 393–400, Mar. 2010, doi: 10.1016/J.CEJ.2009.11.025.
- [385] D. A. Musale and A. Kumar, "Effects of surface crosslinking on sieving characteristics of chitosan/poly(acrylonitrile) composite nanofiltration membranes," *Sep Purif Technol*, vol. 21, no. 1–2, pp. 27–37, 2000, doi: 10.1016/S1383-5866(00)00188-X.
- [386] A. O. Almatouq, A.; Babatunde, "Concurrent phosphorus recovery and energy generation in mediator-less dual chamber microbial fuel cells: Mechanisms and influencing factors," *Int. J. Environ. Res. Public Health*, vol. 13, p. 375, 2016, doi: <https://doi.org/10.3390/ijerph13040375>.

- [387] Zhang Ge, Zhen. He, “Long performance of 200L microbial fuel cell treating municipal wastewater: treatment, energy and cost,” *Environ sci water Res tech*, vol. 2, pp. 274–281, 2016.
- [388] I. You, J.; Greenman, J.; Melhuish, C.; Ieropoulos, “Electricity generation and struvite recovery from human urine using microbial,” *J. Chem. Technol. Biotechnol*, vol. 91, pp. 647–654, 2016.
- [389] A. Firdous, S.; Jin, W.; Shahid, N.; Bhatti, Z.A.; Iqbal, A.; Abbasi, U.; Ali, “The performance of microbial fuel cells treating vegetable oil industrial wastewater,” *Environ. Technol. Innov*, vol. 10, pp. 143–151, 2018.
- [390] F. Sciarria, T.P.; Vacca, G.; Tambone, F.; Trombino, L.; Adani, “Nutrient recovery and energy production from digestate using microbial electrochemical technologies (METs),” *J. Clean.Prod*, vol. 206, pp. 1022–1029, 2019.
- [391] H. Wang, Y.; Lin, Z.; Su, X.; Zhao, P.; Zhou, J.; He, Q.; Ai, “Cost-effective domestic wastewater treatment and bioenergy recovery in an immobilized microalgal-based photoautotrophic microbial fuel cell (PMFC),” *Chem. Eng. J*, vol. 372, pp. 956–964, 2019.
- [392] A. Ismail and Y. W. Kee, “Investigation on voltage loss mechanism for direct methanol fuel cell,” *Energy Reports*, vol. 10, pp. 535–543, Nov. 2023, doi: 10.1016/J.EGYR.2023.06.029.
- [393] S. V. Raghavulu, P. S. Babu, R. K. Goud, G. V. Subhash, S. Srikanth, and S. V. Mohan, “Bioaugmentation of an electrochemically active strain to enhance the electron discharge of mixed culture: process evaluation through electro-kinetic analysis,” *RSC Adv*, vol. 2, no. 2, pp. 677–688, Dec. 2011, doi: 10.1039/C1RA00540E.
- [394] P. Mishra, P. Sudarsanam, D. M. Mahapatra, A. Elmekawy, D. Pant, and L. Singh, “Progressions in cathodic catalysts for oxygen reduction and hydrogen evolution in bioelectrochemical systems: Molybdenum as the next-generation catalyst,” *Catal Rev Sci Eng*, vol. 65, no. 3, pp. 986–1078, Jul. 2023, doi: 10.1080/01614940.2021.
- [395] S. Venkata Mohan and S. Srikanth, “Enhanced wastewater treatment efficiency through microbially catalyzed oxidation and reduction: Synergistic effect of biocathode microenvironment,” *Bioresour Technol*, vol. 102, no. 22, pp. 10210–10220, Nov. 2011, doi: 10.1016/J.BIORTECH.2011.08.034.
- [396] S. Zinadini, A. A. Zinatizadeh, M. Rahimi, V. Vatanpour, and Z. Rahimi, “High power generation and COD removal in a microbial fuel cell operated by a novel sulfonated PES/PES blend proton exchange membrane,” *Energy*, vol. 125, pp. 427–438, Apr. 2017, doi: 10.1016/J.ENERGY.2017.02.146.
- [397] S. A. Erenler, T. Unver, B. F. Ozaslan, S. Koytepe, and S. Sezer, “Development of microbial chondroitin sulfate-based proton exchange membranes for microbial fuel cells,” *Fuel*, vol. 363, p. 130976, May 2024, doi: 10.1016/J.FUEL.2024.130976.
- [398] Z. Hu, Q. Liu, Q. Zhang, J. Zhang, L. Chen, and S. Xu, “Facile fabrication of regenerated cellulose-based separators for high-performance lithium-ion batteries by regulating degrees of polymerization,” *Int J Biol Macromol*, vol. 268, p. 131854, May 2024, doi: 10.1016/J.IJBIOMAC.2024.131854.

- [399] “Low-cost crosslinked PVA membranes as alternative proton exchange membrane in hemodialysis wastewater fed bioelectrochemical fuel cells,” *Process Safety and Environmental Protection*, vol. 196, p. 106915, Apr. 2025, doi: 10.1016/J.PSEP.2025.106915.
- [400] P. J. Sarma and K. Mohanty, “Development and comprehensive characterization of low-cost hybrid clay based ceramic membrane for power enhancement in plant based microbial fuel cells (PMFCs),” *Mater Chem Phys*, vol. 296, p. 127337, Feb. 2023, doi: 10.1016/J.MATCHEMPHYS.2023.127337.
- [401] J. Ai *et al.*, “Marangoni-driven self-assembly of hierarchical PAO/PVA membranes for highly efficient uranium extraction from seawater,” *National Science Open*, vol. 4, no. 4, p. 20250024, Jul. 2025, doi: 10.1360/NSO/20250024.
- [402] A. Otálora, T. A. Lerma, Y. Arrieta-Urango, and M. Palencia, “Emerging organic pollutants in aqueous environments: Detection, monitoring, and removal techniques,” *Journal of Science with Technological Applications*, vol. 10, pp. 92–153, May 2021, doi: 10.34294/J.JSTA.21.10.68.
- [403] N. Aarab, A. Hsini, A. Essekri, M. Laabd, R. Lakhmiri, and A. Albourine, “Removal of an emerging pharmaceutical pollutant (metronidazole) using PPY-PANi copolymer: Kinetics, equilibrium and DFT identification of adsorption mechanism,” *Groundw Sustain Dev*, vol. 11, Oct. 2020, doi: 10.1016/J.GSD.2020.100416.
- [404] Q. Wu, S. Jiao, M. Ma, and S. Peng, “Microbial fuel cell system: a promising technology for pollutant removal and environmental remediation,” *Environmental Science and Pollution Research*, vol. 27, no. 7, pp. 6749–6764, Mar. 2020, doi: 10.1007/S11356-020-07745-0.
- [405] Z. Entemake, “Review of emerging contaminants sources, effects, and removal methods,” *Applied and Computational Engineering*, vol. 56, no. 1, pp. 52–59, Apr. 2024, doi: 10.54254/2755-2721/56/20240614.
- [406] F. Tarrass, O. Benjelloun, M. B. - nefrologia, “Towards zero liquid discharge in hemodialysis. Possible issues,” 2021
- [407] L. Winchell, M. Wells, J. Ross, ... X. F.-S. of T. T., and undefined 2021, “Analyses of per-and polyfluoroalkyl substances (PFAS) through the urban water cycle: Toward achieving an integrated analytical workflow across aqueous,” *Elsevier LJ Winchell, MJM Wells, JJ Ross, X Fonoll, JW Norton Jr, S Kuplicki, M Khan, KY Bell Science of The Total Environment*, 2021 Nov. 15, 2025.
- [408] C. Nassour, S. Nabhani-Gebara, S. J. Barton, and J. Barker, “Anti-cancer drug waste disposal practices and wastewater management in hospitals: A Lebanese survey,” *Journal of Oncology Pharmacy Practice*, 2024, vol. 30, no. 1, pp. 78–87, Jan. 2024, doi: 10.1177/10781552231167875.
- [409] S. Hussain, G. S.-S. W. M. in the Tourism, and undefined 2025, “Sustainable Waste Management Practices in the Hospitality Industry: Towards Environmental Responsibility and Economic Viability,” pp. 91–124, Jan. 2024, doi: 10.4018/979-8-3693-6110-8.CH005.
- [410] P. Del Vecchio, N. Haro, ... F. S.-W. S. and, and undefined 2019, “Ampicillin removal by adsorption onto activated carbon: kinetics, equilibrium and thermodynamics,” *Water Science and Technology*, 2019

- [411] A. Mestre, J. Pires, J. Nogueira, ... J. P.-B., and undefined 2009, "Waste-derived activated carbons for removal of ibuprofen from solution: role of surface chemistry and pore structure," Nov. 15, 2025.
- [412] X. Zhu, Y. Wang, R. Sun, D. Z.- Chemosphere, and undefined 2013, "Photocatalytic degradation of tetracycline in aqueous solution by nanosized TiO₂ Chemosphere. 2013 Aug;92(8):925-32. doi: 10.1016/j.chemosphere.2013.02.066. Epub 2013 Mar 27. PMID: 23541148
- [413] D. Balarak, M. Baniasadi, S. Lee, M. S.-D. and Water, and undefined 2021, "Ciprofloxacin adsorption onto Azolla filiculoides activated carbon from aqueous solutions," Nov. 15, 2025.
- [414] S. Carabineiro, T. Thavorn-Amornsri, M. P.-W. research, and undefined 2011, "Adsorption of ciprofloxacin on surface-modified carbon materials," *Water Research*, 2011
- [415] M. Hassan, S. Kanwal, R. Singh, ... M. S.-I. J. of, and undefined 2024, "Current challenges and future perspectives associated with configuration of microbial fuel cell for simultaneous energy generation and wastewater treatment," *International Journal of Hydrogen Energy*, 2024
- [416] A. Nawaz, I. ul Haq, K. Qaisar, B. Gunes, ... S. R.-P. S. and, and undefined 2022, "Microbial fuel cells: Insight into simultaneous wastewater treatment and bioelectricity generation," Nov. 15, 2025.
- [417] K. Zhang *et al.*, "Enhanced the treatment of antibiotic wastewater and antibiotic resistance genes control by Fe⁰-catalyzed microalgal MFCs in continuous flow mode," *Journal of Water Process Engineering*, 2023 Nov. 15, 2025.
- [418] X. Yang, Q. Wang, T. Li, H. Xu, H. S.-B. Technology, and undefined 2022, "Antibiotic removal and antibiotic resistance genes fate by regulating bioelectrochemical characteristics in microbial fuel cells," *Bioresource Technology*, 2022 Nov. 15, 2025.
- [419] S. Li *et al.*, "Sustainable conversion of antibiotic wastewater using microbial fuel cells: Energy harvesting and resistance mechanism analysis," *Chemosphere*, 313, 137584.
- [420] M. Ghasemi *et al.*, "Nano-structured carbon as electrode material in microbial fuel cells: A comprehensive review," *J Alloys Compd*, vol. 580, pp. 245–255, Dec. 2013, doi: 10.1016/J.JALLCOM.2013.05.094.
- [421] M. M. Hossain *et al.*, "Per- and polyfluoroalkyl substances (PFAS) exposure in biota and remediation strategies: Toxicological and biochemical perspectives," *Journal of Hazardous Materials Advances*, vol. 17, Feb. 2025, doi: 10.1016/J.HAZADV.2024.100579.
- [422] A. Roy *et al.*, "Eco-engineered N-Methyl-2-pyrrolidone-free antibacterial chitosan/cellulose acetate membrane separator for real hospital wastewater-fed microbial fuel cells," *Next Research*, vol. 2, no. 4, p. 100867, Dec. 2025, doi: 10.1016/J.NEXRES.2025.100867.
- [423] A. Seilkhan, "An Overview of Green Applications of Natural Products for Pharmaceutical, Biofuel, and Rubber Industries: Case Study of Kazakh Dandelion (*Taraxacum kok-saghyz* Rodin)," *ES Energy and Environment*, vol. 25, Sep. 2024, doi: 10.30919/ESEE1171.
- [424] Y. H.-C. S. Reviews and undefined 2014, "Key advances in the chemical modification of nanocelluloses," *Chemical Society Reviews*, 2014

- [425] S. Kumar, P. Shukla, K. Das, V. K.-I. J. of Biological, "Chitosan/water caltrop pericarp extract reinforced active edible film and its efficacy as strawberry coating for prolonging shelf life," *International Journal of Biological Macromolecules*, 307 (2025): 142115
- [426] P. Gu *et al.*, "Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution," *Environmental pollution* 240 (2018): 493-505.
- [427] G. Zhao, X. Huang, Z. Tang, Q. Huang, F. N.-P. Chemistry, "Polymer-based nanocomposites for heavy metal ions removal from aqueous solution: a review," *Polymer Chemistry*, 9(26), pp.3562-3582.
- [428] A. de Moraes, P. Andrade, ... A. de F.-C., and undefined 2015, "Fabrication of transparent and ultraviolet shielding composite films based on graphene oxide and cellulose acetate," *Carbohydrate polymers* 123 (2015): 217-227.
- [429] M. Sharma, P. Mondal, A. D. Sontakke, A. Chakraborty, and M. K. Purkait, "High performance graphene-oxide doped cellulose acetate-based ion exchange membrane for environmental remediation applications," *Int J Environ Anal Chem*, vol. 103, no. 19, pp. 7751-7772, Dec. 2023, doi: 10.1080/03067319.2021.1975276
- [430] S. M. Ghaseminezhad, M. Barikani, and M. Salehirad, "Development of graphene oxide-cellulose acetate nanocomposite reverse osmosis membrane for seawater desalination," *Compos B Eng*, vol. 161, pp. 320-327, Mar. 2019, doi: 10.1016/J.COMPOSITESB.2018.10.079.
- [431] L. Xu *et al.*, "Hydrophobic Graphene Oxide as a Promising Barrier of Water Vapour for Regenerated Cellulose Nanocomposite Films," *ACS Omega*, vol. 4, no. 1, pp. 509-517, Jan. 2019, doi: 10.1021/ACSOMEGA.8B02866.
- [432] A. H. Jawad, A. S. Abdulhameed, A. Reghioa, and Z. M. Yaseen, "Zwitterion composite chitosan-epichlorohydrin/zeolite for adsorption of methylene blue and reactive red 120 dyes," *Int. J. Biol. Macromol.*, vol. 163, pp. 756-765, Nov. 2020, doi: 10.1016/j.ijbiomac.2020.07.014.
- [433] A. S. Eltaweil, E. M. Abd El-Monaem, G. M. El-Subriti, B. M. Ali, M. M. Abd El-Latif, and A. M. Omer, "Graphene oxide incorporated cellulose acetate beads for efficient removal of methylene blue dye; isotherms, kinetic, mechanism and co-existing ions studies," *Journal of Porous Materials* 2022 30:2, vol. 30, no. 2, pp. 607-618, Oct. 2022, doi: 10.1007/S10934-022-01347-6.
- [434] Y. Wang *et al.*, "Enhancing the permeability and selectivity of graphene oxide membrane through polyhedral oligomeric silsesquioxane intercalation for textile wastewater treatment," *Desalination*, vol. 587, p. 117933, Oct. 2024, doi: 10.1016/J.DESAL.2024.117933.
- [435] N. El-Shafai, M. El-Khouly, M. E.-K.-R., and undefined 2018, "Graphene oxide-metal oxide nanocomposites: fabrication, characterization and removal of cationic rhodamine B dye," *RSC advances* 8, no. 24 (2018): 13323-13332.
- [436] N. El-Shafai, M. El-Khouly, M. El-Kemary, M. R.-R., and undefined 2019, "Graphene oxide decorated with zinc oxide nanoflower, silver and titanium dioxide nanoparticles: fabrication, characterization, DNA interaction, and antibacterial," *RSC advances*, 9(7), 3704-3714.
- [437] A. S. Eltaweil, E. M. Abd El-Monaem, G. M. El-Subriti, B. M. Ali, M. M. Abd El-Latif, and A. M. Omer, "Graphene oxide incorporated cellulose acetate beads for efficient removal of

- methylene blue dye; isotherms, kinetic, mechanism and co-existing ions studies,” *Journal of Porous Materials* 2022 30:2, vol. 30, no. 2, pp. 607–618, Oct. 2022, doi: 10.1007/S10934-022-01347-6.
- [438] S. Wang, G. Liu, and J. Pu, “Enhancement of the Strength of Biocomposite Films via GrapheneOxide Modification” (2018): 6321-6331
- [439] E. B. Kim *et al.*, “Antifouling microfiltration membrane filter based on acetylated cellulose ether using vapour-induced phase separation,” *Cellulose*, vol. 31, no. 1, pp. 479–495, Jan. 2024, doi: 10.1007/S10570-023-05650-6
- [440] N. S. Jamaluddin *et al.*, “Exploring Potential of Adsorptive-Photocatalytic MolybdenumDisulphide/Polyacrylonitrile (MoS₂/PAN) Nanofiber Coated Cellulose Acetate (CA) Membranes for Treatment of Wastewater,” *J Polym Environ*, vol. 30, no. 12, pp. 5290–5300, Dec. 2022, doi: 10.1007/S10924-022-02619-7.
- [441] D. S. Lim *et al.*, “Highly miscible bio-based poly (lactic acid)/acetylated cellulose ether ultrafiltration membranes with improved water permeances,” *J Memb Sci*, vol. 711, p. 123195, Nov. 2024, doi: 10.1016/J.MEMSCI.2024.123195.
- [442] E. Vasconcelos, F. da Luz, ... S. da P.-J. of M, “Nanostructured 3D bioprinting of PLA with bioglass-CNT scaffolds for osseus tissue graft manufacturing,” *Journal of Materials Research and Technology*, 23, 5923-5938
- [443] A. Pandele, A. Constantinescu, I. Radu, F. M.- Materials, and undefined 2020, “Synthesis and characterization of pla-micro-structured hydroxyapatite composite films,” *Materials* 13.2 (2020): 274.
- [444] O. S. Serbanescu, A. M. Pandele, M. Oprea, A. Semenescu, V. K. Thakur, and S. I. Voicu, “Crown Ether-Immobilized Cellulose Acetate Membranes for the Retention of Gd (III),” *Polymers* 2021, Vol. 13, Page 3978, vol. 13, no. 22, p. 3978, Nov. 2021, doi: 10.3390/POLYM13223978.
- [445] M. Oprea, A. M. Pandele, A. I. Nicoara, A. Nicolescu, C. Deleanu, and S. I. Voicu, “Crown ether- functionalized cellulose acetate membranes with potential applications in osseointegration,” *Int J Biol Macromol*, vol. 230, p. 123162, Mar. 2023, doi: 10.1016/J.IJBIOMAC.2023.123162.
- [446] A. Choudhury *et al.*, “Effect of electrode surface properties on enhanced electron transfer activity in microbial fuel cells,” *Eng Life Sci*, vol. 17, no. 2, pp. 186–192, Feb. 2017, doi: 10.1002/ELSC.201600063.
- [447] Q. Fang, X. Zhou, W. Deng, Z. Zheng, and Z. Liu, “Freestanding bacterial cellulose-graphene oxide composite membranes with high mechanical strength for selective ion permeation,” *Sci Rep*, vol. 6, Sep. 2016, doi: 10.1038/SREP33185.
- [448] G. Palanisamy, Y. M. Im, A. P. Muhammed, K. Palanisamy, S. Thangarasu, and T. H. Oh, “Fabrication of Cellulose Acetate-Based Proton Exchange Membrane with Sulfonated SiO₂ and Plasticizers for Microbial Fuel Cell Applications,” *Membranes* 2023, Vol. 13, Page 581, vol.13, no. 6, p. 581, Jun. 2023, doi: 10.3390/MEMBRANES13060581.
- [449] T. Gabryś, B. Fryczkowska, U. Jančić, J. Trček, and S. Gorgieva, “GO-Enabled Bacterial CelluloseMembranes by Multistep, In Situ Loading: Effect of Bacterial Strain and Loading Pattern on Nanocomposite Properties,” *Materials* 2023, Vol. 16, Page 1296, vol. 16, no. 3, p. 1296, Feb. 2023, doi: 10.3390/MA16031296.

- [450] H. Luo *et al.*, “Layer-by-layer assembled bacterial cellulose/graphene oxide hydrogels with extremely enhanced mechanical properties,” vol. 10, no. 3, Sep. 2018, doi: 10.1007/S40820-018-0195-3.
- [451] E. Rashidian, V. Babaeipour, A. Chegeni, N. Khodamoradi, and M. Omid, “Synthesis and characterization of bacterial cellulose/graphene oxide nano-biocomposites,” vol. 42, no. 9, pp. 4698–4706, Sep. 2021, doi: 10.1002/PC.26179.
- [452] F. G. Torres, O. P. Troncoso, D. Lopez, C. Grande, and C. M. Gomez, “Reversible stress softening and stress recovery of cellulose networks,” *Soft Matter*, vol. 5, no. 21, pp. 4185–4190, 2009, doi: 10.1039/B900441F.
- [453] X. Wang *et al.*, “Preparation, characterisation, and desalination performance study of cellulose acetate membranes with MIL-53(Fe) additive,” *J Memb Sci*, vol. 590, p. 117057, Nov. 2019, doi: 10.1016/J.MEMSCI.2019.04.061.
- [454] G. Abbas, A. H. Tunio, K. R. Memon, A. A. Mahesar, F. H. Memon, and G. R. Abbasi, “Modification of Cellulose Ether with Organic Carbonate for Enhanced Thermal and Rheological Properties: Characterization and Analysis,” *ACS Omega*, vol. 8, no. 28, pp. 25453–25466, Jul. 2023, doi: 10.1021/ACSOMEGA.3C02974.
- [455] Y. Zhou *et al.*, “Simultaneous electricity production and antibiotics removal by microbial fuel cells,” *J Environ Manage*, vol. 217, pp. 565–572, Jul. 2018, doi: 10.1016/J.JENVMAN.2018.04.013.
- [456] S. J. Huang, K. A. Dwivedi, S. Kumar, C. T. Wang, and A. K. Yadav, “Binder-free NiO/MnO₂ coated carbon-based anodes for simultaneous norfloxacin removal, wastewater treatment and power generation in dual-chamber microbial fuel cell,” *Environmental Pollution*, vol. 317, p. 120578, Jan. 2023, doi: 10.1016/J.ENVPOL.2022.120578.
- [457] A. Roy, S. Kumar, A. Kumar, A. Ebihara, C. T. Wang, and V. Katiyar, “Bioinspired electrodes and microbiome synergy: Driving next-generation green energy in benthic plant microbial fuel cells – A comprehensive review,” *Next Energy*, vol. 10, p. 100485, Jan. 2026, doi: 10.1016/J.NXENER.2025.100485.
- [458] T. Hua, S. Li, F. Li, B. S. Ondon, Y. Liu, and H. Wang, “Degradation performance and microbial community analysis of microbial electrolysis cells for erythromycin wastewater treatment,” *Biochem Eng J*, vol. 146, pp. 1–9, Jun. 2019, doi: 10.1016/J.BEJ.2019.02.008.
- [459] N. Udomkittayachai, W. Xue, K. Xiao, C. V.-W. Research, and undefined 2021, “Electroconductive moving bed membrane bioreactor (EcMB-MBR) for single-step decentralized wastewater treatment: Performance, mechanisms, and cost,” *Water Research*, 188, 116547.
- [460] R. Wang *et al.*, “A novel reduced graphene oxide/polypyrrole conductive ceramic membrane enhanced electric field membrane bioreactor: Mariculture wastewater treatment,” *Bioresour Technol*, 376, 128917.
- [461] Y. Zhou *et al.*, “Simultaneous electricity production and antibiotics removal by microbial fuel cells,” *J Environ Manage*, vol. 217, pp. 565–572, Jul. 2018, doi: 10.1016/J.JENVMAN.2018.04.013.

- [462] B. Neethu, G. D. Bhowmick, and M. M. Ghangrekar, "A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell," *Biochem Eng J*, vol. 148, pp. 170–177, Aug. 2019, doi: 10.1016/J.BEJ.2019.05.011.
- [463] W. Chen, Z. Liu, Y. Li, X. Xing, Q. Liao, and X. Zhu, "Improved electricity generation, coulombic efficiency and microbial community structure of microbial fuel cells using sodium citrate as an effective additive," *J Power Sources*, vol. 482, p. 228947, Jan. 2021, doi: 10.1016/J.JPOWSOUR.2020.228947.
- [464] W. Yang, X. Wang, M. Son, B. L.-J. of P. Sources, and undefined 2020, "Simultaneously enhancing power density and coulombic efficiency with a hydrophobic Fe–N4/activated carbon air cathode for microbial fuel cells," *Journal of Power Sources*, 465, 228264.
- [465] B. Neethu, G. Bhowmick, M. G.-B. Engineering, and undefined 2019, "A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell," *Biochemical Engineering Journal*, 148, 170-177.
- [466] S. Chen, S. A. Patil, and U. Schröder, "Substrate crossover effect and performance regeneration of the biofouled rotating air-cathode in microbial fuel cell," *Front Energy Res*, vol. 6, no. SEP, p. 410182, Sep. 2018, doi: 10.3389/FENRG.2018.00085/BIBTEX.
- [467] S. Chen, S. A. Patil, and U. Schröder, "Substrate crossover effect and performance regeneration of the biofouled rotating air-cathode in microbial fuel cell," *Front Energy Res*, vol. 6, no. SEP, p. 410182, Sep. 2018, doi: 10.3389/FENRG.2018.00085/BIBTEX.
- [468] Y. Fan, H. Hu, and H. Liu, "Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration," *J Power Sources*, vol. 171, no. 2, pp. 348–354, Sep. 2007, doi: 10.1016/J.JPOWSOUR.2007.06.220.
- [469] A. N. Ghadge and M. M. Ghangrekar, "Development of low cost ceramic separator using mineral cation exchanger to enhance performance of microbial fuel cells," *Electrochim Acta*, vol. 166, pp. 320–328, Jun. 2015, doi: 10.1016/J.ELECTACTA.2015.03.105.
- [470] J. Ramirez-Nava *et al.*, "The Implications of Membranes Used as Separators in Microbial Fuel Cells," *Membranes (Basel)*, vol. 11, no. 10, p. 738, Oct. 2021, doi: 10.3390/MEMBRANES11100738.
- [471] S. M. Lyth *et al.*, "Graphene Oxide for Proton Exchange Membrane and Anion Exchange Membrane Fuel Cells," *ECS Meeting Abstracts*, vol. MA2016-02, no. 38, p. 2550, Sep. 2016, doi: 10.1149/MA2016-02/38/2550.
- [472] Y. Wang, W. Li, G. Sheng, B. Shi, H. Y.-W. research, and undefined 2013, "In-situ utilization of generated electricity in an electrochemical membrane bioreactor to mitigate membrane fouling," In *Development of Novel Bioelectrochemical Membrane Separation Technologies for Wastewater Treatment and Resource Recovery* (pp. 123-136). Singapore: Springer Singapore.
- [473] L. R. Teixeira, C. M. Cordas, M. P. Fonseca, N. E. C. Duke, P. R. Pokkuluri, and C. A. Salgueiro, "Modulation of the Redox Potential and Electron/Proton Transfer Mechanisms in the Outer Membrane Cytochrome OmcF From *Geobacter sulfurreducens*," vol. 10, Jan. 2020, doi: 10.3389/FMICB.2019.02941/FULL.

- [474] L. R. Teixeira, J. M. Dantas, C. A. Salgueiro, and C. M. Cordas, "Thermodynamic and kinetic properties of the outer membrane cytochrome OmcF, a key protein for extracellular electrontransfer in *Geobacter sulfurreducens*," *Biochim Biophys Acta Bioenerg*, vol. 1859, no. 10, pp. 1132–1137, Oct. 2018, doi: 10.1016/J.BBABIO.2018.07.007.
- [475] K. Vimal and R. B. V. Appa, "Chemically modified biopolymer as an eco-friendly corrosion inhibitor for mild steel in a neutral chloride environment," *New Journal of Chemistry*, vol. 41, no. 14, pp. 6278–6289, Jul. 2017, doi: 10.1039/C7NJ00553A.
- [476] M. GENÇTEN, K. DÖNMEZ, and Y. ŞAHİN, "Investigation of the temperature effect on electrochemical behaviors of TiO₂ for gel type valve regulated lead-acid batteries," *ANADOLU UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY A - Applied Sciences and Engineering*, vol. 17, no. 5, pp. 882–882, Dec. 2016, doi: 10.18038/AUBTDA.279856.
- [477] J. Philips, K. Verbeeck, K. Rabaey, and J. B. A. Arends, "Electron transfer mechanisms in biofilms," *Microbial Electrochemical and Fuel Cells: Fundamentals and Applications*, pp. 67–113, Jan. 2016, doi: 10.1016/B978-1-78242-375-1.00003-4.
- [478] F. Rezaei, T. L. Richard, R. A. Brennan, and B. E. Logan, "Substrate-Enhanced Microbial FuelCells for Improved Remote Power Generation from Sediment-Based Systems," *Environ SciTechnol*, vol. 41, no. 11, pp. 4053–4058, Jun. 2007, doi: 10.1021/ES070426E.
- [479] P. Devi, H. Mehta, U. Batra, and G. Kaur, "Utilization of superhydrophilic metallosurfactantelectrocatalyst for enhanced cathodic oxygen reduction reaction in Microbial Fuel Cell," *JPower Sources*, vol. 628, p. 235841, Feb. 2025, doi: 10.1016/J.JPOWSOUR.2024.235841.
- [480] O. Guadarrama-Pérez *et al.*, "Variation of graphene/titanium dioxide concentration as electrocatalyst for an oxygen reduction reaction in constructed wetland-microbial fuel cells," *Electrochem commun*, vol. 157, p. 107618, Dec. 2023, doi: 10.1016/J.ELECOM.2023.107618.
- [481] E. M. Conners, K. Rengasamy, and A. Bose, "Electroactive biofilms: how microbial electron transfer enables bioelectrochemical applications," *J Ind Microbiol Biotechnol*, vol. 49, no. 4, p. kuac012, Jul. 2022, doi: 10.1093/JIMB/KUAC012.
- [482] J. Philips, K. Verbeeck, K. Rabaey, and J. B. A. Arends, "Electron transfer mechanisms in biofilms," *Microbial Electrochemical and Fuel Cells: Fundamentals and Applications*, pp. 67–113, Jan. 2016, doi: 10.1016/B978-1-78242-375-1.00003-4.
- [483] B. Das, S. S. Gaur, A. R. Katha, C. T. Wang, and V. Katiyar, "Crosslinked poly(vinyl alcohol) membrane as separator for domestic wastewater-fed dual chambered microbial fuel cells," *IntJ Hydrogen Energy*, vol. 46, no. 10, pp. 7073–7086, Feb. 2021, doi: 10.1016/J.IJHYDENE.2020.11.213.
- [484] N. Ranjbaran, A. Akbari, R. Yegani, H. Roghani-Mamaqani, and M. Chapalaghi, "Graphene oxide decorated copper nanoparticles embedded polysulfone nanocomposite membrane: Anti-bacterial, organo-bio fouling evaluation in pharmaceutical wastewater treatment via MBR," *Journal of Industrial and Engineering Chemistry*, vol. 142, pp. 293–308, Feb. 2025, doi:10.1016/J.IJEC.2024.07.036.
- [485] V. Ravikumar, I. Mijakovic, and S. Pandit, "Antimicrobial Activity of Graphene Oxide Contributes to Alteration of Key Stress-Related and Membrane Bound Proteins," *Int JNanomedicine*, vol. 17, p. 6707, 2022, doi: 10.2147/IJN.S387590.

- [486] Y. Zhang *et al.*, “Hydrophilic and antimicrobial properties of hydroxypropyl trimethyl ammonium chloride chitosan/graphene oxide membrane for dye rejection,” *Journal of Water Process Engineering*, vol. 67, p. 106220, Nov. 2024, doi: 10.1016/J.JWPE.2024.106220.
- [487] C. Geng *et al.*, “Anti-biofouling property and anti-leaching investigation of modifier for PVDF ultrafiltration membrane by incorporating antibacterial graphene oxide derivatives,” *J Environ Chem Eng*, vol. 10, no. 6, p. 108558, Dec. 2022, doi: 10.1016/J.JECE.2022.108558.
- [488] M. Zahid *et al.*, “Investigating the Antibacterial Activity of Polymeric Membranes Fabricated with Aminated Graphene Oxide,” *Membranes 2021, Vol. 11, Page 510*, vol. 11, no. 7, p. 510, Jul. 2021, doi: 10.3390/MEMBRANES11070510.
- [489] S. Liu *et al.*, “Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: Membrane and oxidative stress,” *ACS Nano*, vol. 5, no. 9, pp. 6971–6980, Sep. 2011, doi: 10.1021/NN202451X/SUPPL_FILE/NN202451X_SI_001.PDF.
- [490] N. AlQasas and D. Johnson, “Combined Effects of Surface Roughness, Solubility Parameters, and Hydrophilicity on Biofouling of Reverse Osmosis Membranes,” *Membranes (Basel)*, vol. 14, no. 11, p. 235, Nov. 2024, doi: 10.3390/MEMBRANES14110235/S1.
- [491] D. Rana and T. Matsuura, “Surface modifications for antifouling membranes,” *Chem Rev*, vol. 110, no. 4, pp. 2448–2471, Apr. 2010, doi: 10.1021/CR800208Y.

Annexure

Details of the revised contents as per the examiner's comments

Sl. No	Chapter	Original page no	Section/figure	Content removed/modified	Type	Reason for removing
1	3	Page 104	Figure 3.5	Original cyclic voltammetry graph and related interpretation removed and revised	Figure and text	Revised based on examiner comments regarding CV interpretation
2	3	Page 105	Fig 3.6	Tafel plot discussion	Text and Figure	Revised based on examiner comments regarding Tafel interpretation
3	5	Page 105	Figure 5.8	Original cyclic voltammetry graph and related interpretation removed and revised	Figure and text	Revised based on examiner comments regarding CV interpretation
4	5	Page 169	Figure 5.10	Tafel plot discussion	Figure and text	Revised based on examiner comments regarding Tafel interpretation

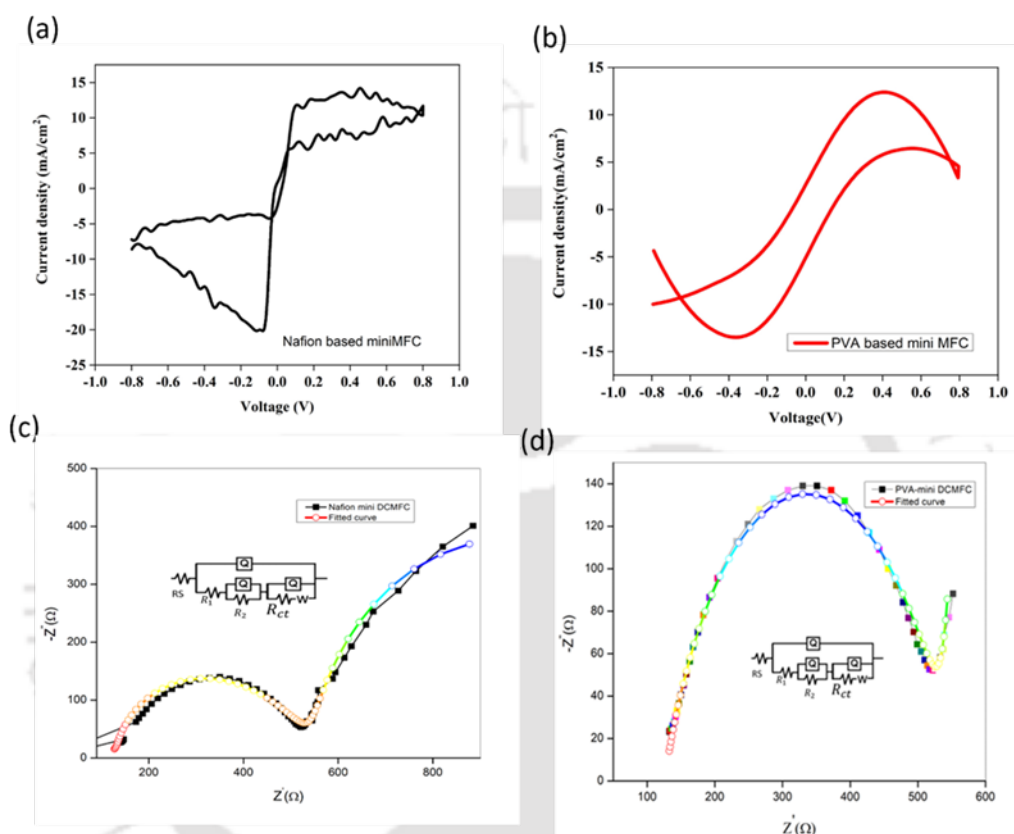
Detailed Removed Figures and content

Removed figure 1

Original location: chapter 3 page 104

Figure No with caption – 3.5 “Biomimetic mini MFC electricity production (a) Nafion-based MFC's cyclicvoltammetry (b), PVA-GA-based mini MFC (c), Nyquist plot PVA-GA mini MFC (d) Nafion-based MFC”

Old picture figure attached bellow-



Removed figure portion – Fig 3.5 (a) Biomimetic mini MFC electricity production (a) Nafion-based MFC's cyclicvoltammetry

Removed text- “This phenomenon was not observed in the Commercial Nafion-based mini DCMFC. The Nafion-based MFC exhibited symmetrical and non-quasi rectangular CV profiles profile indicating stable and reversible electrochemical behaviour. Similar observations have been reported in the literature [13], [14], [15], [16] where deviations from classical electrochemical behaviour were attributed to complex microbial-electrode

interactions in the case of Nafion-based mini DCMFC, whereas a sigmoidal curve is observed in Figure 3.6(b) in the case of PVA-based DCMFC. “

New Figure No and caption – “Figure 3.5. Biomimetic mini MFC electricity production (a) Cyclic voltammetry, PVA-GA-based mini MFC (b) Nyquist plot of Nafion-based MFC (c) PVA-GA-based MFC”

Screenshot of the new figure on the updated revised thesis, now on page 105,

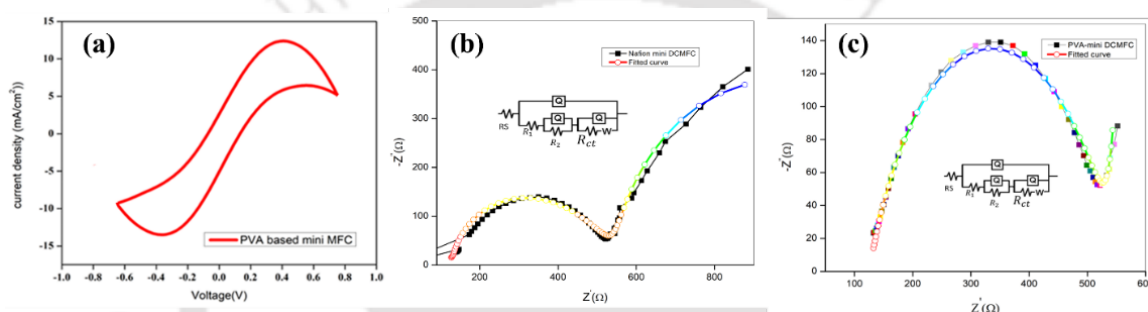


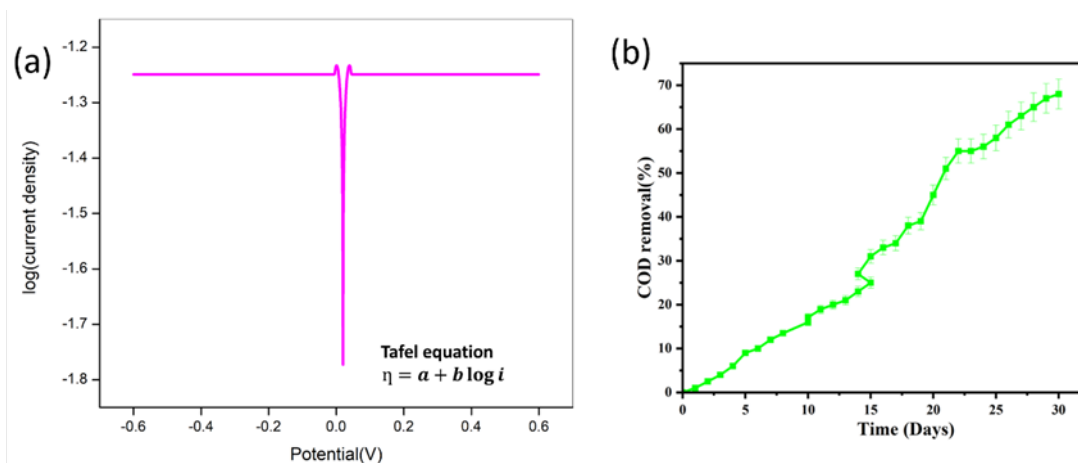
Figure 3.5. Biomimetic mini MFC electricity production (a) Cyclic voltammetry, PVA-GA-based mini MFC (b) Nyquist plot of Nafion-based MFC (c) PVA-GA-based MFC

Removed figure 2

Original location: chapter 3, page 105

Figure No with caption – Figure 3.6. (a) Tafel plot, (b) COD removal by crosslinked PVA-based Mini DCMFC”

Old figure attached below-



Removed figure portion –(a) Tafel plot,

Removed text portion -

“Here, E represents the electrode potential measured with respect to the Ag/AgCl reference electrode during electrochemical measurement. The Tafel analysis was performed to evaluate the electrochemical kinetics of the anode chamber. Based on the equation in Bard and Faulker for the Tafel plot.

Removed figure portion –(a) Tafel plot,

Removed text portion -

“Here, E represents the electrode potential measured with respect to the Ag/AgCl reference electrode during electrochemical measurement. The Tafel analysis was performed to evaluate the electrochemical kinetics of the anode chamber. Based on the equation in Bard and Faulker for the Tafel plot. Tafel equation may be used to mathematically depict the voltage dips brought on by activation losses:

$$\eta = a + b \log i$$

Equation 5

In the given equation, ‘i’ reflects the current in Ampere, ‘E’ represents the electrode potential, and the Tafel analysis is based on overpotential (η), defined as the deviation from the equilibrium potential. The exchange current density (i_0) was obtained by extrapolating the linear Tafel region (η vs $\log i$) to $\eta = 0$. that govern the kinetics of an electron transfer-controlled process. The

Tafel relationship was examined using overpotential (η) instead of applied voltage, consistent with electrochemical theory (Bard and Faulkner) [21]. The exchange current density (i_0) was determined by extrapolating the linear region of the Tafel plot to zero overpotential, as commonly applied in electrochemical and microbial fuel cell studies [22], [23], [24]. The kinetic behaviour of the Tafel analysis observed is consistent with cyclic voltammetry results, indicating active redox processes and EIS showing reduced charge transfer resistance in PVA-based MFC. These values depend on the electrochemical reaction, electrode material, and electrolyte composition. Tafel plots provide a fuel cell's activation losses a visual representation, making it possible to calculate important kinetic characteristics like exchange current density [314]. By extrapolating to $E = 0$, the maximum current achievable with minimal polarization can be determined [315]. The transfer coefficient can be inferred from the slope of the plot. For the miniDCMFC operation, a Tafel plot was constructed (Figure 3.7(a)) to determine kinetic parameters like the oxidative slope. To reduce mass transfer constraints, linear regression analysis was carried out at low potentials (-0.6 to 0.66 V). As previously mentioned, kinetic parameters were calculated using the best fit of numerous linear regressions within this potential range [316]. The lower the activation energy barrier for the forward reaction, the faster the reaction rate, and a larger i_0 indicates this. The equilibrium between forward and reverse electron transfer processes is represented by the electron transfer coefficient, standing at " α ," in the Butler-Volmer model of electrode kinetics [317].

New Figure No and caption – “Figure 3.6. COD removal by crosslinked PVA-based Mini DCMFC” on Page 106

Screenshot of the new figure on the updated revised thesis, now on page 105,

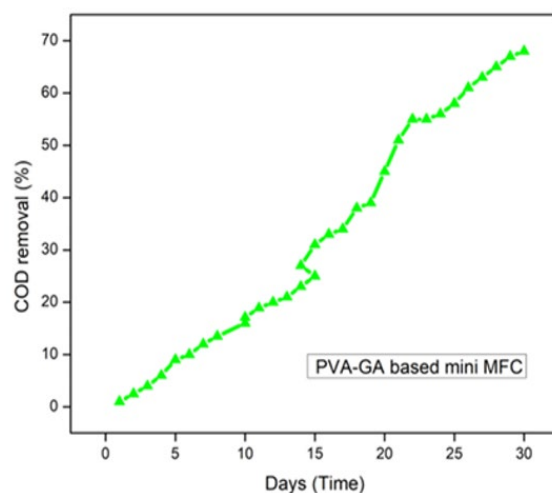
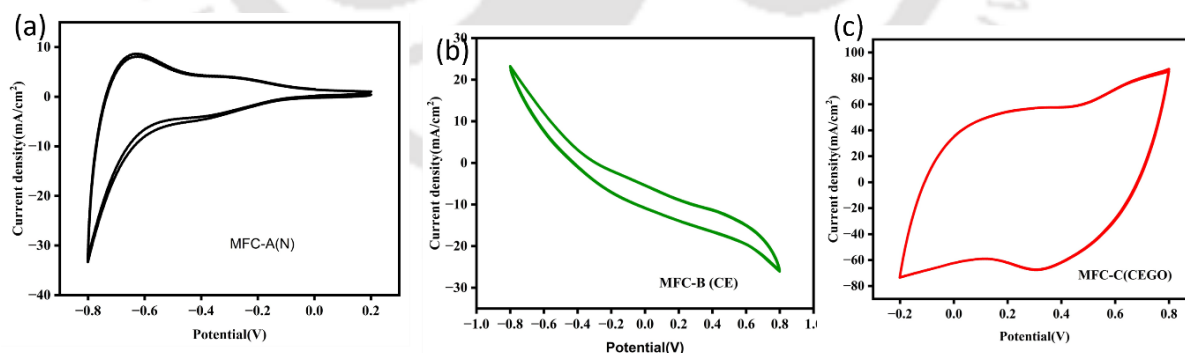


Figure 3.6. COD removal by crosslinked PVA-based Mini DCMFC” on Page 106

Original location : chapter 5 page 168

Figure No with caption – Figure 5.8. Cyclic voltammetry of (a) PFAS Nafion-based, (b) Pristine CE based, (c) GO-modified membrane-based MFCs”

Old figure attached below-



Removed figure portion –Figure 5.8. Cyclic voltammetry of (a) PFAS Nafion-based, (b) Pristine CE-based

Removed text portion -

“Conversely, the commercial Nafion-based MFC-A (N) displayed two separate redox processes linked to the presence of bacterial cells, asseen in Figure 5.8.(a). In comparison to the control MFC-A

(N), these redox peaks are ascribed to the activity of protein molecules with metal centres. The measured redox potentials align closely with the typical potential ranges of cytochromes and iron-sulfur proteins, suggesting that these bacterial redox-active proteins participate in electron transport within the system [82]“

New Figure No and caption – “Figure 5.8. Cyclic voltammetry of GO-modified membrane-based MFCs” on page 167

Screenshot of the new figure on the updated revised thesis, now on page 105,

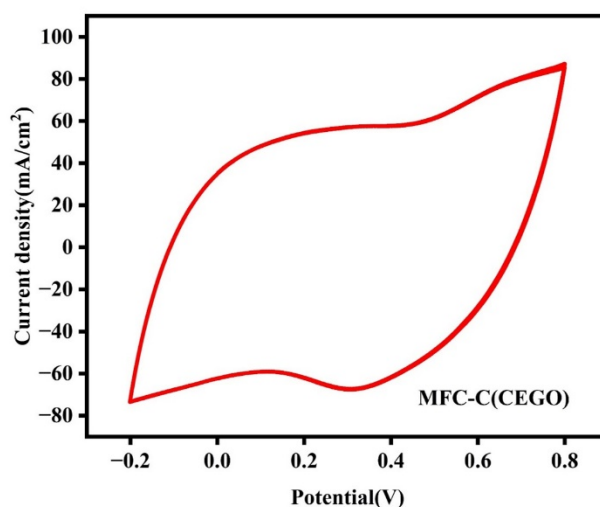


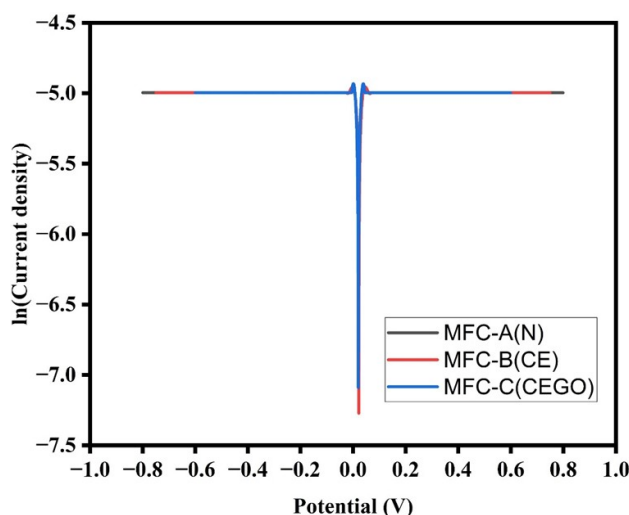
Figure 5.8. Cyclic voltammetry of GO-modified membrane-based MFCs

Removed figure 4

Original location: chapter 5, page 170

Figure No with caption – “Figure 5.10. Tafel plot analysis of the different MFC types with the fabricated membrane”

The old figure attached below is removed-



Removed figure portion –“Figure 5.10. Tafel plot analysis of the different MFC types with the fabricated membrane”

Removed text portion- “The activation barriers that the responding species or biocatalyst must overcome in biochemical and bio-electrochemical processes are very comparable. Tafel polarisation measurements were performed to clarify the ORR catalytic behaviour of the membrane-integrated MFC systems. The resultant charts facilitate the calculation of the exchange current density (J_0), a critical quantity that indicates the inherent rate of electron transport at the electrode interface. Figure 5.10. illustrates that the MFC-C (CEGO-based) configuration exhibits a much greater J_0 compared to MFC-A and MFC-B, indicating superior catalytic activity. MFC-C has the lowest Tafel slope (4.7 mV dec^{-1}), slightly lower than MFC-A (4.9 mV dec^{-1}) and MFC-B (4.6 mV dec^{-1}), indicating enhanced ORR kinetics and decreased activation overpotentials. A similar observation has been made in [88][89].”

Research output

Aparajita Roy, Bhanupriya Das, Sonu Kumar, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, Per and Poly-Fluoroalkyl-Free PVA Membrane Separator for Sustainable Energy Recovery From Municipal Wastewater Using Biomimetic Miniature Microbial Fuel Cell Journal of Applied Polymer Science Volume 142 Issue - 460021-8995 <https://doi.org/10.1002/app.57809>

Aparajita Roy, Sonu Kumar, Bhanupriya Das, Kuhelika Das, Amit Kumar , Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, Eco-engineered N-Methyl-2-pyrrolidone-free antibacterial chitosan/cellulose acetate membrane separator for real hospital wastewater-fed microbial fuel cells, Next Research, Volume 2, Issue 4, 2025, 100867, ISSN 3050-4759, <https://doi.org/10.1016/j.nexres.2025.100867>

Aparajita Roy, Sonu. Kumar, Kuhelika Das, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, “Next-Generation Per and Poly- Fluoroalkyl-Free Graphene Oxide Modified Cellulose Ether Charge Separator for Antibiotic Micropollutant Removal and Energy Recovery in Hospital Wastewater-Fed Microbial Fuel Cell,” Journal of Polymer Science (2026): 118, SN - 2642-4150 <https://doi.org/10.1002/pola.70044>

Aparajita Roy, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, A critical review on advancing bioinspired smart membranes for green energy recovery in microbial fuel cells: Paving the way for a sustainable future, Journal of Environmental Chemical Engineering, Volume 13, Issue 5, 2025, 118094, <https://doi.org/10.1016/j.jece.2025.118094>

Aparajita Roy, Sonu Kumar, Amit Kumar, Akio Ebihara, Chin Tsan Wang, Vimal Katiyar, Bioinspired Electrodes and Microbiome Synergy: Driving Next-Generation Green Energy in Benthic Plant Microbial Fuel Cells - A Comprehensive Review Next Energy volume 10 2026

Awards and Recognitions

Aparajita Roy, Bhanupriya Das, Chin Tsan Wang, Vimal Katiyar Harvesting of energy from real wastewater using micron-scale microbial fuel cell presented in Internal conference on Polymers for Advanced Technology February 23-25, 2023 Goa, India. **Best poster Award in APA 2023 conference**

Aparajita Roy Vimal Katiyar PFAS-Free PVA Biomimetic Separator Enabling Scalable Energy Harvesting in Miniature Microbial Fuel Cells presented in GCDEM 2025, Singapore one North October 16-19, 2025

Aparajita Roy, Vimal katiyar, Energy recovery and optimisation from real wastewater using a micron-scale microbial fuel cell presented in the Research industrial conclave (RIC 2025) conference, October 10-12, 2025, IIT Guwahati, Assam, India

Aparajita Roy , Akio Ebihara , Amit kumar, Vimal Katiyar , Recent review on the advancement of Microbial fuel cell technology from Architectural Design to membrane innovation for energy generation presented in International Conference on Climate Change (ICCC 2024) , 6-8th November 2024, Gifu University, Japan

Aparajita Roy, Bhanupriya Das, chin Tsan Wang, Energy harvesting from wastewater using biodegradable polymer-based microbial fuel cell presented in 17th International Conference on Polymer Science and Technology, December 10-11 2023 Guwahati , India

Aparajita Roy, Bhanupriya Das, Chin Tsan Wang, Vimal Katiyar Harvesting of energy from real wastewater using a micron-scale microbial fuel cell presented in IICHE- CHEMCON December 27-30, 2023, Kolkata, India.

RESEARCH ARTICLE

Per and Poly-Fluoroalkyl-Free PVA Membrane Separator for Sustainable Energy Recovery From Municipal Wastewater Using Biomimetic Miniature Microbial Fuel Cell

Aparajita Roy¹ | Bhanupriya Das¹ | Sonu Kumar¹ | Amit Kumar¹ | Akio Ebihara^{1,2} | Chin Tsan Wang^{1,3} | Vimal Katiyar¹ ¹Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India | ²Faculty of Applied Biological Sciences, Gifu University, Gifu, Japan | ³Department of Mechanical and Electromechanical Engineering, National I-Lan University, Yilan City, Taiwan

Correspondence: Vimal Katiyar (vkatiyar@iitg.ac.in) | Aparajita Roy (r.aparajita@iitg.ac.in)

Received: 9 June 2025 | Revised: 28 July 2025 | Accepted: 31 July 2025

Funding: The authors received no specific funding for this work.

Keywords: biomimetic | biopolymers and renewable polymers | films

ABSTRACT

Microbial fuel cells (MFCs) have emerged as a viable alternative in the search for sustainable bioenergy and efficient wastewater treatment. This work introduces the creation of a biomimetic, miniaturized MFC that utilizes nature-inspired flow channel design and eco-friendly materials to enhance electrochemical performance and reduce overall costs. A micron-scale, heart-shaped flow channel was constructed to provide continuous micromixing of the effluent at both the anode and cathode, enhancing mass transfer, substrate utilization, and bacterial-electrode interactions. A PFAS-free, laboratory-synthesized membrane was used as a charge separator, replacing the conventional Nafion 117 membrane, to eliminate costly and ecologically detrimental components. A custom-designed Arduino-UNO-based smart data recording system was included for real-time voltage monitoring, providing a cost-effective substitute for commercial multimeters. The MFC attained a peak coulombic efficiency of 85.5% and exhibited a concurrent chemical oxygen demand (COD) elimination efficiency of $68\% \pm 0.10\%$ when processing municipal wastewater. A thorough techno-economic study indicated that the overall cost of the system was 46.10 USD/ft², making it around eight times more cost-effective than conventional Nafion-based MFCs. The decrease in costs, together with enhanced electrochemical and treatment efficacy, highlights the system's scalability and practical feasibility for decentralized wastewater treatment and energy production.

1 | Introduction

Water shortages are an escalating worldwide concern impacting billions, exacerbated by climate change, population growth, pollution, and unsustainable water management practices. Comprehending water shortage is essential for developing policy at the global, regional, national, and local levels. The Eighth Phase of the International Hydrological Programme (IHP-VIII), which focuses on "Water Security: Responses to Local, Regional, and Global Challenges (2014–2021)," has six topics, including "addressing water scarcity and quality" [1].

The water supply problem was named the most significant concern of our time in the World Economic Forum's 2015 Global Risks Report [2]. One of the goals of the newly established Sustainable Development Goals by the United Nations is to "significantly reduce the number of people suffering from water scarcity" [2015] [3]. Pollution from industrial waste, agricultural runoff, and inadequate sanitation further reduces usable freshwater supplies. To combat this crisis, sustainable solutions like wastewater treatment are essential. Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic organic compounds characterized by the partial or complete



Eco-engineered N-Methyl-2-pyrrolidone-free antibacterial chitosan/cellulose acetate membrane separator for real hospital wastewater-fed microbial fuel cells

Aparajita Roy^{a,d}, Sonu Kumar^{a,d}, Bhanupriya Das^b, Kuhelika Das^c, Amit Kumar^{a,d}, Akio Ebihara^{a,e}, Chin Tsan Wang^{a,f}, Vimal Katiyar^{a,d,*}

^a Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India

^b Institute of Environmental Engineering and Management, National Taipei University of Technology, Taipei 10608, Taiwan

^c Department of Bioscience and Bioengineering, Indian Institute of Technology Guwahati, Assam, India

^d Center for Sustainable Polymer, Indian Institute of Technology Guwahati, India

^e Faculty of Applied Biological Sciences, Gifu University, Japan

^f Department of Mechanical and Electromechanical Engineering, National I-Lan University, Taiwan

ARTICLE INFO

Keywords

Microbial fuel cell
Hospital wastewater treatment
Bio-composite membrane
Chitosan
Organic matter removal

ABSTRACT

Hospital wastewater (HWW) comprises a complex amalgamation of pharmacologically active substances and toxic contaminants, presenting threats to ecosystems and human health. Inadequate treatment may result in water contamination and the spread of infectious illnesses. Microbial Fuel Cells (MFCs) provide an efficient method for treating HWW by utilizing organic-rich contaminants as substrate while producing bioelectricity. The present study produced a cost-effective, environmentally friendly bio-composite membrane composed of cellulose acetate (CA) and chitosan (CS) as an alternative to PFAS-based membranes such as Nafion. The CA-CS membrane was synthesised using glutaraldehyde (GA) crosslinking, which reduced free hydroxyl groups and established ether and acetal connections, therefore improving chemical and mechanical stability. The membrane demonstrated superior physicochemical characteristics, with a tensile strength of 32.47 ± 1.30 MPa and an elongation at break of 161.47 ± 8.07 %, hence assuring durability under operational stress and resistance to biofouling. Electrochemical Impedance Spectroscopy (EIS) demonstrated a minimal charge transfer resistance of 3.8Ω , resulting in a substantial exchange current density of 1.2 mA/m^2 , signifying effective electron transfer and catalytic performance. In hospital wastewater-fed MFCs, the CA-CS membrane attained a Coulombic efficiency of 92.18 % and a COD removal efficiency of 83.4 ± 0.10 %. The membrane production procedure used water as a solvent, so removing harmful chemicals and activation stages, thereby promoting green synthesis. A techno-economic study calculated the manufacturing cost at 45.62 USD/m², making it 6.87 times more cost-efficient than Nafion-based membranes. This environmentally sustainable and cost-effective membrane provides a viable alternative for real-field HWW treatment and renewable energy production.

1. Introduction

The main goal of waste management is to reduce the negative effects of garbage on the environment and public health. Hospital wastewaters (HWW) exhibit qualitative similarities to municipal wastewaters; nonetheless, they include harmful and infectious chemicals and compounds that pose risks to environmental health, the safety of personnel in these facilities, and the broader community. Hospital effluents include various substances used in medical, laboratory, and research

applications, together with human excreta. This includes both insoluble and soluble organic and inorganic pollutants, which are very harmful to people and aquatic organisms even at minimal doses, and are categorized as biologically active chemicals. Furthermore, HWW retains residual low-grade heat from pharmaceutical processes, which may be used to enhance microbial activity and increase the ionic conductivity of the MFC's membrane, hence optimising system performance [1]. Hospital wastewater (HWW) is generally released into Wastewater Treatment Plants (WWTPs) and co-treated with urban wastewater (UWW) in

* Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India.
E-mail address: vkatiyar@iitg.ac.in (V. Katiyar).

<https://doi.org/10.1016/j.nexres.2025.100867>

Received 14 August 2025; Received in revised form 8 September 2025; Accepted 25 September 2025

Available online 1 October 2025

3050-4759/© 2025 Published by Elsevier Ltd.

RESEARCH ARTICLE

Next-Generation Per and Poly-Fluoroalkyl-Free Graphene Oxide Modified Cellulose Ether Charge Separator for Antibiotic Micropollutant Removal and Energy Recovery in Hospital Wastewater-Fed Microbial Fuel Cell

Aparajita Roy^{1,2}  | Sonu Kumar^{1,2} | Kuhelika Das³ | Amit Kumar^{1,2} | Akio Ebihara⁴ | Chin Tsan Wang⁵ | Vimal Katiyar^{1,2}

¹Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India | ²Center for Sustainable Polymer, Indian Institute of Technology Guwahati, Guwahati, Assam, India | ³Department of Bioscience and Bioengineering, Indian Institute of Technology Guwahati, Guwahati, Assam, India | ⁴Faculty of Applied Biological Sciences, Gifu University, Gifu, Japan | ⁵Department of Mechanical and Electromechanical Engineering, National I-Lan University, Ilan, Taiwan

Correspondence: Vimal Katiyar (vkatiyar@iitg.ac.in)

Received: 3 December 2025 | Revised: 16 December 2025 | Accepted: 18 December 2025

Keywords: ampicillin removal | cellulose ether | microbial fuel cell | micropollutant | PFAS-free separator | wastewater treatment

ABSTRACT

The increasing prevalence of pharmaceutical pollutants, especially antibiotics like ampicillin, in aquatic environments necessitates novel treatment approaches that integrate pollutant removal with resource recovery. Traditional PFAS-based membranes, such as Nafion, frequently used in microbial fuel cells (MFCs), present environmental concerns due to their persistence and toxicity. This study introduces a graphene oxide (GO)-modified cellulose ether membrane, characterized by antifouling properties, as a PFAS-free alternative, and thoroughly evaluates its dual function of ampicillin elimination and bioelectricity generation from hospital wastewater. Physicochemical characterization revealed that the incorporation of GO improved membrane hydrophilicity and mechanical stability, leading to a 2.53-fold increase in tensile strength compared to pure cellulose ether, while concurrently reducing substrate crossing. In a MFC, the CEGO membrane facilitated increased microbial electroactivity and improved electron transfer, achieving a maximum current density of 86.6 mA cm⁻². This enhanced electrochemical performance, coupled with a columbic efficiency of 59.3%, was succeeded by a substantial ampicillin degradation of 96.2%, thereby underscoring the relationship between optimized proton transport and strengthened microbe-electrode interactions. Furthermore, the membrane exhibited operational stability under high-COD conditions typical of hospital wastewater, indicating considerable structural resilience and potential for extended application in sustainable wastewater treatment and energy recovery.

1 | Introduction

The increasing worldwide issues of environmental contamination have always been a central subject of scientific research and politics. Although traditional pollutants like heavy metals and persistent organic pollutants have been rigorously monitored, a new category of chemicals, referred to as emerging pollutants (EPs) or contaminants of emerging concern, has

attracted considerable attention in recent decades. EPs are characterized as manmade or naturally occurring substances that are not regularly monitored or governed by existing environmental legislation. They provide a potential or established harm to natural ecosystems and human health [1]. These compounds, including medications, personal care products (PCPs), endocrine-disrupting chemicals (EDCs), pesticides, and industrial additives, result from contemporary urban,