Sustainable Materials and Technology

Akil Ahmad
Mohamad Nasir Mohamad Ibrahim
Asim Ali Yaqoob
Siti Hamidah Mohd Setapar
Editors

Microbial Fuel Cells for Environmental Remediation

Springer

Sustainable Materials and Technology

Sustainable Materials and Technology (SMT) book series publishes research monographs (both edited and authored volumes) showcasing the latest developments in the field and comprehensively covering topics such as:

- Recycling of waste into useful material and their energy applications
- Catalytic action of Nano oxides for efficient carbon reforming process
- Sustainable technologies for plastic transformation
- Bifunctional nanoparticles for sustainable water splitting applications
- Sustainable dying and printing
- New materials from waste
- Sustainable Manure Management and Technology: Potentials, Uses and limitations
- Sustainable Mechanical Engineering Approach
- Sustainable biochemistry for the improvement of health
- Sustainable development of Mechanical recycling of automotive components
- Sustainable waste recycling and conversion in useful materials for different applications
- Sustainable development of inexpensive Nano-photo catalysts
- Sustainable development of recycling of discarded lithium ion batteries
- Modern sustainable cement and concrete
- Sustainable adsorbent for hazardous removal
- Sustainable superior electromagnetic shielding materials
- Excellent sustainable nanostructured materials for energy storage device
- Sustainable development of heavy metal detoxification from water
- Carbon dioxide utilization for sustainable energy
- Sustainable development in green syntheses of materials
- Environment friendly and sustainable cloth for garments application
- Sustainable design and application of eco-materials
- Nanoparticles for sustainable environment applications
- Sustainable remediation of industrial contaminated water towards potential industrial applications
- Biomaterials for sustainable bioremediations

Akil Ahmad · Mohamad Nasir Mohamad Ibrahim ·
Asim Ali Yaqoob · Siti Hamidah Mohd Setapar
Editors

Microbial Fuel Cells for Environmental Remediation

Springer

Editors
Akil Ahmad
Department of Chemistry
College of Science and Humanities
Prince Sattam Bin Abdulaziz University
Al-Kharj, Saudi Arabia

Asim Ali Yaqoob
School of Chemical Sciences
Universiti Sains Malaysia
Penang, Malaysia

Mohamad Nasir Mohamad Ibrahim
School of Chemical Sciences
Universiti Sains Malaysia
Penang, Malaysia

Siti Hamidah Mohd Setapar
Malaysia-Japan International Institute
of Technology
Universiti Teknologi Malaysia
Kuala Lumpur, Malaysia

ISSN 2731-0426 ISSN 2731-0434 (electronic)
Sustainable Materials and Technology
ISBN 978-981-19-2680-8 ISBN 978-981-19-2681-5 (eBook)
https://doi.org/10.1007/978-981-19-2681-5

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Dedication

The editors are honored to dedicate this book to Mrs. Sajada Begum and Mr. Shakil Ahmad (Beloved Mother and Brother of Dr. Akil Ahmad)

and

Dr. Mohamad Nasir parents Saniah Abd Hamid and S. Mohamad Ibrahim Seeni Mohamad. May Allah SWT forgive their small and big mistakes and give them a higher place in Jannatul Firdous. Ameen.

Preface

MFCs are developing and noteworthy method that convert chemical energy into electrical energy using bacteria that serve as catalysts. However, MFCs have not yet been applied at a commercial scale due to their low energy production. Due to their sustainability, microbial fuel cells (MFCs) have been recognized as a viable technology for producing energy and removing toxic pollutants from wastewater resources. This approach has attracted attention for its capacity to generate renewable energy and treat wastewater instantaneously.

The unique properties and breakthrough performance of microbial fuel cells classified as high-profile techniques for a broad range of applications in wastewater and environmental fields. Accordingly, researchers have used it as a successful alternative primarily in environmental remediation and energy generation. The increasing number of publications and patents in recent years emphasize the significance of microbial fuel cells in aforementioned areas. This book covers not only the conventional microbial fuel cell applications but also covers the advanced polymer-based electrode materials and their application in environmental and energy applications. Furthermore, the transportation of electrons from bacteria to the electrode surface is an essential step for energy generation. Hence, the poor transportation of electrons may greatly hinder the performance of MFCs. The major fields of applications of microbial fuel cells in environmental and energy fields are discussed in detail.

This book covers the fundamentals of microbial fuel cells and electrodes along with their synthesis, characterization, and potential applications in environmental and energy areas. The book provides significant coverage of the commercial status, trends, and performance of MFCs.

We are greatly thankful to all qualified researchers, scholars, and leading experts for contributing their valuable work. The chapters provided cutting-edge up-to-date research findings on the MFCs. We collected all the information given by eminent authors on MFCs and related research from Turkey, India, Malaysia, Saudi Arabia,

Nigeria, Ghana, Japan, Pakistan, and Bangladesh and finally compiled this project in a fruitful way.

Al-Kharj, Saudi Arabia — Akil Ahmad
Penang, Malaysia — Mohamad Nasir Mohamad Ibrahim
Penang, Malaysia — Asim Ali Yaqoob
Kuala Lumpur, Malaysia — Siti Hamidah Mohd Setapar

Contents

About the Editors

Dr. Akil Ahmad currently working at Prince Sattam bin Abdulaziz University, Saudi Arabia as Assistant Professor in Chemistry and having the experience of seven years as Research Fellow, Teaching Fellow, Postdoc and Visiting Researcher from Universiti Teknologi Malaysia, Universiti Sains Malaysia, University of KwaZulu-Natal, South Africa and Universiti Kebangsaan Malaysia, Malaysia. He has completed Ph.D. in Analytical Chemistry (2011) with the topic "Modification of resin for their use in the separation, preconcentration and determination of metal ions" from Aligarh Muslim University (AMU), India. His research interest in the areas of environmental pollutants and their safe removal, synthesis of nanoparticles and Nanosorbents (GO, CNT), photo-degradation and antimicrobial effects, water and wastewater treatment and adsorption and ion-exchange. He has published more than 100 research articles and chapters in the journals and publishers of international repute such as Scientific reports, Talanta, Chemical Engineering Journal, Journal of Industrial and Engineering Chemistry, Journal of Molecular Liquids, etc. He has also edited five books of Springer and Elsevier. H-index and citation in Scopus are 22 and 1827 and in Google scholar, H-index and citation are 25 and 2404. He is guest editor of many reputed journal namely *Adsorption Science and Technology*-Hindawi, *Polymers* MDPI, *Frontiers in Environmental Chemistry* and *Journal of Chemistry*, Hindawi.

Dr. Mohamad Nasir Mohamad Ibrahim obtained his B.Sc. (1994), M.Sc. (1997) and Ph.D. (1999) from Missouri S&T (formerly known as University of Missouri-Rolla, USA). He is currently served as an Associate Professor in the School of Chemical Sciences, Universiti Sains Malaysia (USM). He had published more than 120 journal articles, 17 book chapters and 5 academic books throughout his twenty-year career in USM including "Graphene: A Versatile Advanced Material". Currently his Scopus h-index is 35 with 4026 citations and he had been granted with ten patents for his R&D products/processes where five of them are at an international level. More than thirty research grants (1 international grant and 5 industry grants) were secured and utilized to support his team's research activities. He had received fourteen international awards for his research outputs and currently serve as a Guest Editor for Frontiers in Chemistry. He had supervised more than 20 graduate students. His main research areas are Lignin and Lignocellulosic Materials, Nanoparticles, Graphene & Biomaterials and Petroleum Engineering. Recently, he is busy working in the microbial fuel cells topic especially in developing a novel electrode and had published several papers in well reputed journals such as Chemical Engineering Journal, Journal of Cleaner Production, etc. At the moment he is the pioneer on MFCs research topic in the School of Chemical Sciences, USM. He enjoys sharing his industrial experience, where he spent two and half years worked as a R&D Manager at NSE Resources Corporation Sdn Bhd., in his classes.

Dr. Asim Ali Yaqoob obtained his B.Sc. (2010), M.Sc. (2014) and M.Phil (2018) from Mirpur University of Science and Technology Mirpur, Mirpur, 10250, Ajk-Pakistan. Recently he completed his Ph.D. (2021) from School of Chemical Sciences, Universiti Sains Malaysia (USM) under the supervision of Dr. Mohamad Nasir Mohamad Ibrahim. His area of interest is energy generation coupled with wastewater treatment and currently his project is on Microbial Fuel Cells. He has published 22 articles in high reputed journals and several book chapters. He also a co-author for an academic book (Graphene: A Versatile Advanced Material) published by USM Press, Malaysia. He has completed M.Phil in

Material Chemistry (2018) with the topic of "Designing and characterizing of Ag@Polycarbazole nanocables" from Mirpur University of Science and Technology (MUST), AJK Pakistan. His Google scholar H-index and citation is 14 and 695 respectively and has filed one patent for an industrial process. He also invited reviewer of many reputed international journals such as Nanotechnology Reviews, International Journal of Energy Research, Journal of Chemistry, PLOS ONE and many others. As a part of academic work, he has different collaborations with well-known research labs in the world. He enjoys sharing his industrial experience, where he spent one year worked as a research assistant at Ekahala Resources Sdn Bhd, Malaysia.

Dr. Siti Hamidah Mohd Setapar is an academician at Malaysia-Japan International Institute of Technology and a research fellow at Centre of Lipid Engineering and Applied Research, Universiti Teknologi Malaysia. Her research interests' are extraction of various colorants from natural source such as leave, plants and local flowers; and micellar nanotechnology. Dr. Siti Hamidah pursues her Master degree at Universiti Teknologi Malaysia with her thesis "Penicilin G Extraction using Reverse Micelle Extraction Extraction Sytem" and then continue her Doctor of Philosophy degree at Loughborough University, United Kingdom with thesis title "Reverse Micelle Liquid-Liquid Extraction of a Pharmaceutical Product".

Dr. Siti Hamidah has been working in micellar nanotechnology, environmental pollutants removal, adsorption area. She has written 60 journal papers, won 50 innovation awards, awarded RM 2 million of research grants, and successfully secured four commercialization grants amounting RM 1 million to put her products further in the market. She has been coached by Barbara Diehl (Innovation Academy, Dublin), BioEconomy Corporation, CEO of Al-Ikhsan Sports and Kosmetik Alwan, Platcom Ventures, Cradle, TERAJU, and Micheal Herrera (Branding Consultant). She obtained many supports from various agencies and with that, she is now focusing on realizing her dream to provide high quality-affordable products for her society

that is based from her expertise in micellar nanotechnology. H-index and citations in Google Scholar are 22 and 2037.

Basic Introduction to Microbial Fuel Cells

M. Azizul Moqsud

1 What is Microbial Fuel Cell?

The Microbial Fuel Cell (MFC) is a bio-electrochemical device which is used to generate electricity in other words; MFC is a kind of bio-electrochemical fuel cell system that generates bioelectricity by the metabolic activities of the microorganisms [1–5]. The generated electricity by the decomposing organic substance travels from anode to cathode through an external circuit [6–9]. MFC is a promising technology for renewable energy production in specific applications such as remediation of pollution or cleaning up the wastewater. There are many other applications of MFCs in the field of energy and environment [10–15]. In microbial fuel cell, the organic substances are degraded by the microorganisms and hence produce the electron. The external circuit connected with an anode and cathode is placed to collect this electron and continue the current. In the previous research, it was observed that this MFC method can be used to clean the wastewater, bioremediated sulfide contaminated sediment, and consequently bioelectricity generation. The benefit of this method is that it can generate bioelectricity while cleaning the environment [16–19]. Moqsud et al. [3] showed that MFC can also generate electricity from the organic waste in a compost type MFC. Since then, other researchers are trying to use this novel technology to generate bioelectricity by recycling the organic waste [4, 5, 20–23]. Figure 1 shows the schematic diagram of the microbial fuel cell which was used in the laboratory. The anode and cathode relate to the external circuit. The resistance was also used to complete the external circuit for the power output.

M. A. Moqsud (✉)
Department of Civil and Environmental Engineering, Yamaguchi University, Yamaguchi, Japan
e-mail: azizul@yucivil.onmicrosoft.com

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_1

2 Major Parts of a Microbial Fuel Cell

2.1 Essential Components of MFCs

The main three components of the MFC are anode, cathode, and if needed the membrane or the separator. The anode is developed with different carbon type materials. Figure 1 shows the different types of anode materials such as carbon fiber, carbon felt, and bamboo charcoals. The shape of the anode materials is also varied. For the case of cathode, it is also possible to use the same materials as anode. However, as it was mentioned before cathode needs some oxygen to generate the electricity. So, the cathode chamber should be provided with the oxygen. The separator of the MFC is related to the membrane of the MFC. This part is costly as most of the time the separator is made of high-cost membrane which ultimately decrease the sustainability of the total process.

Among all shaped MFCs, the cube reactor is popular among the researchers due to its user-friendly anode and cathode chambers. Single chamber and double chamber MFCs are developed for the research purpose of the wastewater treatment. However, the shape of the MFC reactor is varied based on its purpose and the materials used inside the reactor such as rectangular shaped, circular shaped, and cylindrical shaped. Figure 2 shows the schematic diagram of the MFC which is generally used with the solid biomass. The anode and cathode are separated by the biomass and most of the time the specific separator does not need to explore the bioelectricity generation. As mentioned earlier, the separator did not need for all different types of MFCs.

There are different types of Microbial Fuel Cells. The single chamber and the double chamber microbial fuel cell are the common types of microbial fuel cells [24–29]. Normally, the single chamber MFC has two parts such as the anode part and cathode part [1, 4, 30–33]. The anode part is responsible for the more production of electricity as the electrons are released in this part due to the biodegradation of the

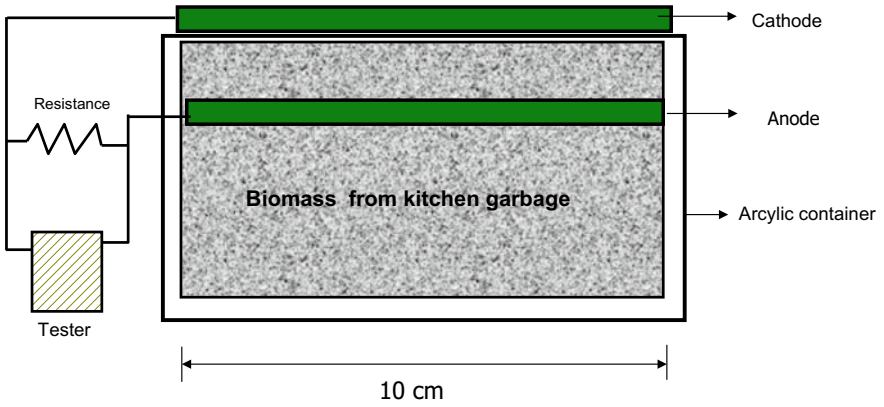

Fig. 1 Schematic diagram of microbial fuel cell. Adapted from Ref. [11] with penance permission

organic matters. The cathode part is the part in where the electron receives the oxygen and produce the water molecule. Normally, it is designed as a manner so that it can receive the oxygen properly. Most of the time, the cathode is placed on the surface to get enough oxygen during the process of bioelectricity generation [34–36]. Secondly, another important part of MFC is the electrode materials and their connection with the copper wire. The external circuit made of the copper wire, resister, and data logger is another major component for electricity generation from the MFC [37–41]. The MFC cell is normally an enclosed cell in where the biomass and other organic substances can be set up. The biomass, sediment, and soil are placed inside the cell. Sometimes, there are covers on the surface of the cell to protect it from the external disturbances [42–44]. Microbial fuel cell can be made in different ways. If it is made for plant microbial fuel cell (PMFC) then plant will be an essential part of that MFC [4]. In the case of the sediment microbial fuel cell (SMFC), the sediment will be the essential part of it (Moqsud 201). Nevertheless, the main objective of all the MFCs is to generate bioelectricity with the help of the bacteria and the major components are the same or nearly similar to all of the different types of MFCs. Figure 2 shows

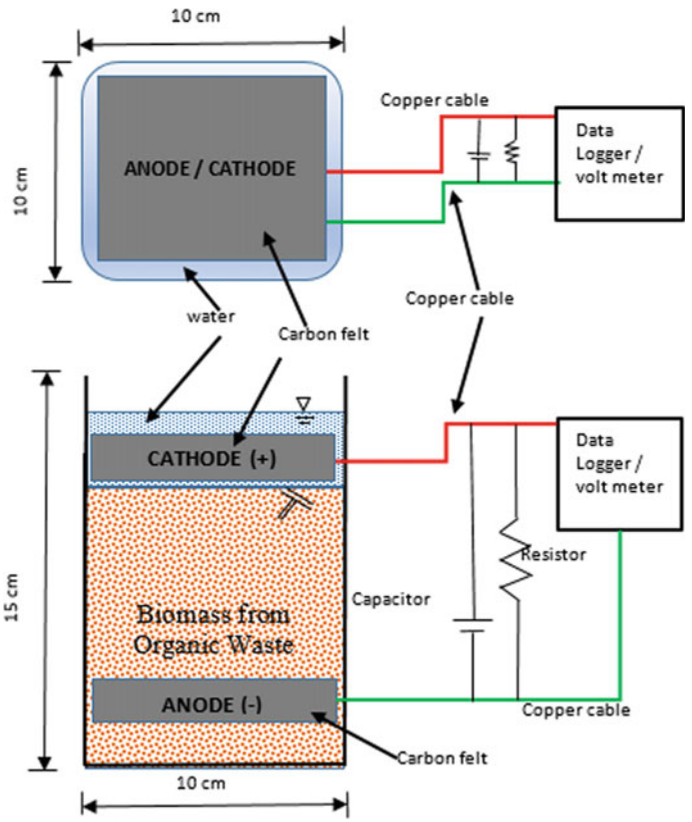

Fig. 2 Schematic diagram of the MFC showing its different parts

the schematic diagram of the microbial fuel cell. It is seen that the essential parts of the MFC is not much changed from the MFC showed earlier; however, it has some other important parts which are widely used. The additional things added in plant microbial fuel cell (PMFC) are plants and the sun. Both the sun and the plants are important parts of the PMFC. Microbes and the electromotive bacteria are also very important parts of the power generation from the microbial fuel cell. The various geo-bacteria, *Shewanella,* and the other microbes play a major role to generate the bioelectricity generation.

2.2 Electrode Materials Used in the Microbial Fuel Cell

Generally, the carbon materials are used for the microbial fuel cells. The reason of using the carbon materials is that it is a conductive material, and it can be a durable material. The carbon material is very good and does not react much with the other materials even in the different medium [45, 46]. Commonly used electrode materials are carbon fiber, carbon felt, graphite felt, carbon brush, and carbon cloth. The different types of carbon materials are used for the different types of purposes. To choose the best carbon material is one of the challenges for the construction of an efficient microbial fuel cell in different environmental conditions. Some researchers use bamboo charcoals as the electrode materials in the MFC [47–50].

3 Common Types of Microbial Fuel Cell According to Their Uses

There are different types of microbial fuel cells. Some MFCs are used for wastewater treatment, and some MFCs are used for bioremediation of contaminated soil or sediments. The main thing of the MFCs is the objective of its use and the medium of their uses. For example, if it is used for treatment of wastewater then it is used under the water environment. However, if it is used for soil/sediment then it can be used as the soil environmental condition. The name of the microbial fuel cell is referred to its uses such as if it is used in the sediment then it is called sediment microbial fuel cell (SMFC) as shown in Fig. 3.

3.1 Sediment Microbial Fuel Cell

In sediment microbial fuel cell, the anode is set inside the sediment and the cathode is set at the surface of the sediment. The organic matters are broken down by the geo-bacteria and the sulphate reducing bacteria (SRB) in the sediment and consequently

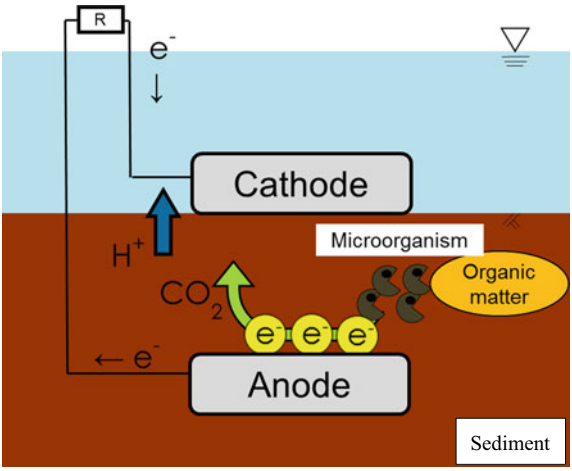

Fig. 3 Schematic diagram of the sediment microbial fuel cell (SMFC)

electron releases. The electron transfers from the anode to cathode and therefore electricity generates. The cathode is placed on the surface or near the surface of the sediment. The availability of oxygen needs to be confirmed at the cathode areas. The benefit of this type of MFC is the ability of purifying the contamination while generating the electricity which was found by Moqsud and Khong. Figure 3 shows the schematic diagram of the sediment microbial fuel cell.

3.2 Plant Microbial Fuel Cells (PMFCs)

Plant microbial fuel cells (PMFCs) are the kind of sediment microbial fuel cell in where plant is used to supply the bioelectricity [4]. The mechanism of plant microbial fuel cell is very interesting. The green leaves get the sunlight from the sun and produces the carbohydrates due to photosynthesis. The generated carbohydrates go to the root zone. More than 60% of the total generated carbohydrates are released at the rhizosphere in the nature. For this reason, the number of geo-bacteria are more in this area. The geo-bacteria use these carbohydrates as the food and grow their numbers. Electron is released while breaking this carbohydrate. The anode catches this electron and travels it to the cathode. This generates the bioelectricity in the plant microbial fuel cell. Figure 4 illustrates the schematic diagram of the plant microbial fuel cell. It is shown that the due to photosynthesis, carbohydrates are produced in the green leaves. The excess amount of carbohydrates are released to the root areas and the geo-bacteria break down this carbohydrate due to their regular activities at the rhizosphere.

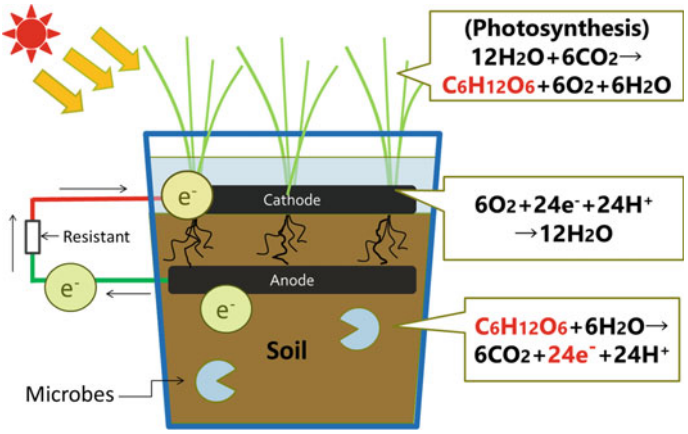

Fig. 4 Schematic diagram of the plant microbial fuel cell

3.3 Solid Waste Microbial Fuel Cells

The MFC in which the organic waste is used as the biomass is solid waste microbial fuel cell. Various types of solid organic waste can be used inside the MFCs. The bioelectricity generation can be possible by using almost all types of organic waste MFCs [50, 51]. Bioelectricity can be also generated by using bamboo waste and the kitchen garbage which has been confirmed in the experiments. This can be reduced the solid waste management problem in the world. The amount to organic waste is the major portion by considering the total solid waste; however, the total organic waste is not recycled properly both in the developing countries as well as industrialized parts of the world. So, if it is possible to generate bioelectricity by using organic waste then it will help to manage the solid waste management problem all over the world. Electricity from landfill leachate using microbial fuel cells has been also studied [30, 52, 53].

4 Energy and Environment

The global energy demand is increasing, and the fossil fuels are decreasing day by day. We need to find the alternate source of energy for the future generation. To get the energy, the greenhouse gas has been released all the time which makes the environmental pollutions when the raw materials are the non-renewable sources. The consequent of this phenomenon is the global warming and the climate change. The trend of climate change is prominent in the recent years. The natural disasters have been increasing, and the loss of life and the properties are increasing in each year. To stop this global warming and climate change phenomenon, the use of environmentally

friendly sources for energy generation must be implemented as soon as possible. To meet the ever-increasing energy demand and to cope with the problems of global warming is the biggest challenges for the scientists and the engineers. Due to the extent of the accident of the nuclear power plant, people are searching for the green source of energy and the safe source of energy in the world in recent time. So, we need both green source of energy and at the same time safe source of energy for the future generation.

5 Future Energy Demand

The mother earth is ready to embrace the 4th industrial revolution now. The earth stands on the brink of a digitalization and technological revolution that will fundamentally change the way we live, work, and relate to one another. The scale, scope, and complexity of this revolution will be so enormous that the mankind did not predict before. The amount of energy demand is increasing faster than ever. Due to the use of internet and the artificial intelligence and wireless sensor networks for the smart cities and the automated automobile the energy demand will be increased soon [54]. The global population is increasing, and many countries are developing in a greater pace. This trend of increasing of energy is alarming and is an alert for the mother nature.

5.1 Renewable Energy's Future

The renewable energy is a good source of green energy which is good for the human and the environment. Solar energy, wind energy, thermal energy, and biofuels are some of the future substitutes of the fossil fuels. However, the current source of renewable energy is unable to meet the needs of the demand for the future. The additional demand may cause another trouble if the technologies will not be expanded. The renewable energy can solve the problem of global warming and the climate change related disasters in the future; however, there are many disadvantages of the renewable energy. The most prominent disadvantage of renewable energy is that it is affected by the weather conditions very much. For example, the solar power cannot work in the rainy days and wind power cannot work when there is no wind flow in the nature. So, the renewable energy will need a lot of development before it has been considered as the major source of green energy [55, 56].

5.2 Biofuels as the Renewable Energy

The first-generation biofuels are the fuels which are generally produced from the food grains such as soybean, corn, sugar cane, and other food products. However, the use of this huge amount of food is not a sustainable solution for the biofuels as there are millions of people who are hungry in the world. It is totally unnecessary to destroy the food products to fuel the car instead of feeding the millions of hungry children. The second-generation biofuel which is mainly by the different kinds of organic waste is not suitable and sustainable solutions either. This is because the amount of organic waste is not enough, and it cannot be possible to collect this huge amount of organic waste in a short period of time. The third-generation biofuels are also not popular yet due to the process of collecting the raw sources and the amount of energy collected from the unit amount of sources of algae.

5.2.1 Future of Biofuels

The future of MFCs is promising. The MFC is a green and safe source of energy. The other major benefits of MFCs are they can be used for environmental pollution removal, wastewater treatment, solid waste management, and desalination along with the bioelectricity generation. The MFC needs to be improved for the future and to use it as a large-scale production of the bioelectricity. Another noteworthy benefit of MFC is that it can be used 24 h without being affected by the weather condition or other external factors like other renewable energy. The various types of MFC can be used for the power source to the smart cities monitoring sensors to achieve the sustainable development goals and the 4th industrial revolutions [7, 57].

6 Conclusion and Future of Microbial Fuel Cells

The main objective of MFCs is to get the new source of bioelectricity by using the strength of microbes. Besides generating bioelectricity, MFCs can clean the polluted environment. MFCs can be a source of bioremediation. It can be used for powering the sensors to the smart cities. It can also power the environmental monitoring sensors. So, MFCs could be very essential part of the future generation to reduce the carbon emission and to clean the polluted environment.

References

1. Logan BE (2007) Microbial fuel cells. Wiley, New Jersey, USA
2. Lovley DR (2006) Microbial fuel cells: novel microbial physiologies and engineering approaches. Curr Opin Biotechnol 17:327–332

3. Moqsud MA, Omine K, Yasufuku N, Hyodo M, Nakata Y (2013) MFC for bioelectricity generation from organic waste. Waste Manag 33(11):2465–2471
4. Moqsud MA, Yoshitake J, Bushra Q, Hyodo M, Omine K, Srik D (2015) Compost in plant microbial fuel cell for bioelectricity generation. Waste Manag 36:63–69
5. Yaqoob AA, Khatoon A, Mohd Setapar SH, Umar K, Parveen T, Ibrahim MNM, Ahmad A, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10(8):819
6. Asim AY, Ibrahim MNM, Khalid U, Tabassum P, Akil A, Lokhat D, Siti H (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desal Water Treat 214:379–389
7. Moqsud MA (2020) Bioelectricity generation and remediation of sulfide contaminated tidal flat sediment. Int J Sedim Res 35:91–96
8. Logan BE, Regan JM (2006) Electricity-producing bacterial communities in microbial fuel cells. Trends Microbiol 14:512–518
9. Yaqoob AA, Ibrahim MNM, Umar K (2021) Biomass-derived composite anode electrode: synthesis, characterizations, and application in microbial fuel cells (MFCs). J Environ Chem Eng 9(5):106111
10. Aelterman P, Rabaey K, Pham HT, Boon N, Verstraete W (2006) Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. Environ Sci Technol 40(10):3388–3394
11. Moqsud MA (2021) Strategies of sustainable solid waste management. IntechOpen Publishers, p 129
12. Yaqoob AA, Serrà A, Ibrahim MNM, Yaakop AS (2021) Self-assembled oil palm biomass-derived modified graphene oxide anode: an efficient medium for energy transportation and bioremediating Cd (II) via microbial fuel cells. Arab J Chem 14(5):103121
13. Yaqoob AA, Ibrahim MNM, Yaakop AS (2021) Application of oil palm lignocellulosic derived material as an efficient anode to boost the toxic metal remediation trend and energy generation through microbial fuel cells. J Clean Prod 314:128062
14. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S, Ahmad A (2021) Preparation, characterization, and application of modified carbonized lignin as an anode for sustainable microbial fuel cell. Process Saf Environ Prot 155:49–60
15. Behera M, Ghangrekar MM (2011) Electricity generation in low-cost microbial fuel cell made up of earthenware of different thickness. Water Sci Technol 64:2468
16. Moqsud MA, Gazali TA, Omine K, Nakata Y (2017) Green electricity by water plants in organic soil and marine sediment through microbial fuel cell. Energy Sour Part A: Recov Utiliz Environ Effects 39(2):160–165
17. Bennetto HP, Stirling JL, Tanaka K, Vega CA (1983) Anodic reaction in microbial fuel cells. Biotechnol Bioeng 25:559–568
18. Borole AP, Aaron D, Hamilton CY, Tsouris C (2010) Understanding long-term changes in microbial fuel cell performance using electrochemical impedance spectroscopy. Environ Sci Technol 44(7):2740–2745
19. Yaqoob AA, Guerrero-Barajas C, Ibrahim MNM, Umar K, Yaakop AS (2022) Local fruit wastes driven benthic microbial fuel cell: a sustainable approach to toxic metal removal and bioelectricity generation. Environ Sci Pollut Res 1–16
20. Chen S, Patil SA, Schröder U (2018) A high-performance rotating graphite fiber brush air cathode for microbial fuel cells. Appl Energy 211:1089–1094
21. Choi J, Ahn Y (2013) Continuous electricity generation in stacked air cathode microbial fuel cell treating domestic wastewater. J Environ Manag 130:146–152
22. Corbella C, Puigagut J, Garf M (2017) Life cycle assessment of constructed wetland systems for wastewater treatment coupled with microbial fuel cells. Sci. Total Environ 584–585:355–362
23. Dewan A, Beyenal H, Lewandowski Z (2008) Scaling up microbial fuel cells. Environ Sci Technol 42(20):7643–7648. https://doi.org/10.1021/es800775d
24. Daud NNM, Ahmad A, Yaqoob AA, Ibrahim MNM (2021) Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. Environ Sci Pollut Res 28(44):62816–62827

25. Fan Y, Sharbrough E, Liu H (2008) Quantification of the internal resistance distribution of microbial fuel cells. Environ Sci Technol 42(21):8101–8107
26. Erbay C, Carreon-Bautista S, Sanchez-Sinencio E, Han A (2014) High performance monolithic power management system with dynamic maximum power point tracking for microbial fuel cells. Environ Sci Technol 48:13992–13999
27. Fornero JJ, Rosenbaum M, Cotta MA, Angenent LT (2008) Microbial fuel cell performance with a pressurized cathode chamber. Environ Sci Technol 42(22):8578–8584
28. Fadzli FS, Rashid M, Yaqoob AA, Ibrahim MNM (2021) Electricity generation and heavy metal remediation by utilizing yam (Dioscorea alata) waste in benthic microbial fuel cells (BMFCs). Biochem Eng J 172:108067
29. Moqsud MA, Omine K, Yasufuku N, Bushra QS, Hyodo M, Nakata Y (2015) Bioelectricity from kitchen garbage and bamboo wastes waste. Manag Res 32:124–130
30. Habermann W, Pommer EH (1991) Biological fuel cells with sulfide storage capacity. Appl Microbiol Biotechnol 35(1):128–133
31. He Z, Minteer SD, Angenent LT (2005) Electricity generation from artificial wastewater using an upflow microbial fuel cell. Environ Sci Technol 39(14):5262–5267
32. Hu Z (2008) Electricity generation by a baffle-chamber membraneless microbial fuel cell. J Power Sour 179(1):27–33
33. Khaled F, Ondel O, Allard B (2016) Microbial fuel cells as power supply of a low power temperature sensor. J Power Sour 306:354–360
34. Kim JR, Min B, Logan BE (2005) Evaluation of procedures to acclimate a microbial fuel cell for electricity production. Appl Microbiol Biotechnol 68:23–30
35. Kim IS, Chae KJ, Choi MJ, Verstraete W (2008) Microbial fuel cells: recent advances, bacterial communities and application beyond electricity generation. Environ Eng Res 13:51–65
36. Kumar M, Singh R (2020) Sewage water treatment with energy recovery using constructed wetlands integrated with a bio-electrochemical system. Environ Sci: Water Res Technol 6:795–808
37. Li Y, Wu Y, Liu B, Luan H, Vadas T, Guo W, Li B (2015) Bioresource Technology Self-sustained reduction of multiple metals in a microbial fuel cell—Microbial electrolysis cell hybrid system. Bioresour Technol 192:238–246
38. Liu F, Sun L, Wan J, Shen L, Yu Y, Hu L, Zhou Y (2020) Performance of different macrophytes in the decontamination of and electricity generation from swine wastewater via an integrated constructed wetland-microbial fuel cell process. J Environ Sci 89:252–263
39. Liu W, Cheng S, Sun D, Huang H, Chen J, Cen K, Inhibition of microbial growth on air cathodes of single chamber microbial fuel cells by incorporating enrofloxacin into the catalyst layer
40. Luke WT, et al (2013) A compact versatile microbial fuel cell from paper. Am Soc Mech Eng 55522:V001T01A015
41. Manohar AK, Mansfeld F (2009) The internal resistance of a microbial fuel cell and its dependence on cell design and operating conditions. Electrochim Acta 54:1664–1670
42. Yaqoob AA, Ibrahim MNM, Yaakop AS, Umar K, Ahmad A (2021) Modified graphene oxide anode: A bioinspired waste material for bioremediation of Pb2+ with energy generation through microbial fuel cells. Chem Eng J 417:128052
43. Oh SE, Logan BE (2005) Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Res 39:4673–4682
44. Pamintuan KS, Sanchez KM (2019) Power generation in a plant-microbial fuel cell assembly with graphite and stainless-steel electrodes growing Vigna Radiata. IOP Conf Ser Mater Sci Eng 703:012037
45. Yaqoob AA, Mohamad Ibrahim MN, Umar K, Bhawani SA, Khan A, Asiri AM et al (2021) Cellulose derived graphene/polyaniline nanocomposite anode for energy generation and bioremediation of toxic metals via benthic microbial fuel cells. Polymers 13(1):135
46. Rabaey K, Verstraete W (2005) Microbial fuel cells: novel biotechnology for energy generation. Trends Biotechnol 23:291–298
47. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S (2020) Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview. Biochem Eng J 107779

48. Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C (2021) Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov 101579
49. Rosenbaum M, Zhao F, Schroder U, Scholz F (2006) Interfacing electrocatalysis and biocatalysis with tungsten carbide: a high performance noble-metal-free microbial fuel cell. Angew Chem 45:6658–6661
50. Yaqoob AA, Mohamad Ibrahim MN, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) Recent advances in anodes for microbial fuel cells: an overview. Materials 13(9):2078
51. Yamane T, Yoshida N, Sugioka M (2021) Estimation of total energy requirement for sewage treatment by a microbial fuel cell with a one-meter air-cathode assuming Michaelis-Menten COD degradation. RSC Adv 11(33):20036–20045
52. Varanasi JL, Roy S, Pandit S, Das D (2015) ScienceDirect Improvement of energy recovery from cellobiose by thermophillic dark fermentative hydrogen production followed by microbial fuel cell. Int J Hydrogen Energy 1–11
53. Varanasi JL, Nayak AK, Sohn Y, Pradhan D, Das D (2016) Improvement of power generation of microbial fuel cell by integrating tungsten oxide electrocatalyst with pure or mixed culture biocatalysts. Electrochim Acta 199:154–163
54. Walter XA, Stinchcombe A, Greenman J, Ieropoulos I (2017) Urine transduction to useable energy: a modular MFC approach for smartphone and remote system charging. Appl Energy 192:575–581
55. Wang YX, Ye ZZ, Si CY, Ying YB (2012) Application of aptamer-based biosensors for detection of pathogenic microorganisms. Chin J Anal Chem 40:634–642
56. Yaqoob AA, Ibrahim MNM, Yaakop AS, Ahmad A (2021) Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. Appl Nanosci 11(6):1949–1961
57. Yang Y, Sun G, Xu M (2011) Microbial fuel cells come of age. J Chem Technol Biotechnol 86(5):625–632

Principle and Working Mechanism of Microbial Fuel Cell

Muhammad Farhan Hil Me, Mohd Nur Ikhmal Salehmin, Swee Su Lim, and Hau Seung Jeremy Wong

Abstract As its name implies, a microbial fuel cell (MFC) is a device capable of producing electricity and electrogenesis from the oxidation of substances catalysed by microorganisms. The achievable voltage range from MFC is between 0.3 and 0.7 V. Due to the biological nature of biofilm growth, it is hard to estimate the voltage generation in MFC compared to a chemical fuel cell. One of the ways to estimate the maximum voltage producible by MFC is by determining its maximum electromotive force (E_{emf}). The value obtained theoretically can be established as a ceiling for the producible cell voltage. However, through empirical study, the obtainable potential is much lower due to potential losses attributed to various factors. Due to different substrates and materials used, the combination of different anodic and cathodic potentials will also affect the maximum obtainable power owing to inherent conductivity differences. By disconnecting the resistor in MFC, open-circuit voltage (OCV) with a value approaching the theoretical E_{emf} can be obtained. The difference in value can be used to pinpoint the cause of potential losses, either from the anode or cathode side. Electrogenesis in MFC relies on the electron produced by microorganisms. As of present, three methods of electron migration method have been theorised: through mediators and electron shuttles, C-type cytochromes and nanowires. The migration can be either through electron hopping or electron delocalisation through nanowires, depending on the microorganism species.

M. F. Hil Me · M. N. I. Salehmin (✉) · S. S. Lim
Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
e-mail: ikhmal@ukm.edu.my

M. F. Hil Me
e-mail: p94598@siswa.ukm.edu.my

S. S. Lim
e-mail: limss@ukm.edu.my

H. S. J. Wong
School of Biological Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
e-mail: jeremywong@student.usm.my

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_2

Keywords Electrogenesis · Thermodynamic · Electron shuttle · Cytochrome · Nanowire

1 Introduction

Microbial fuel cells (MFCs) are devices that oxidise organic and inorganic substances and produce electricity using microorganisms as catalysts. Electrons released by bacteria from various substrates are delivered to the anode (negative terminal) and flow to the cathode (positive terminal) through a conductive substance including a resistor, or the system is operated under a load (i.e., creating energy to power a device) (Fig. 1). Figure 1 shows the operational principle of a microbial fuel cell. A layer of biofilm is grown on the anode surface called bioanode catalysing substrate oxidation reaction. Electrons collected from the reaction are sent to the cathode as driven by electromotive force between anode and cathode through an external circuit. A positive current, by convention, travels from the positive to the negative terminal in the opposite direction of electron transport. The device must be capable of constantly or intermittently replenishing the substrate oxidised at the anode; otherwise, the system is termed as biobattery, which requires further regeneration.

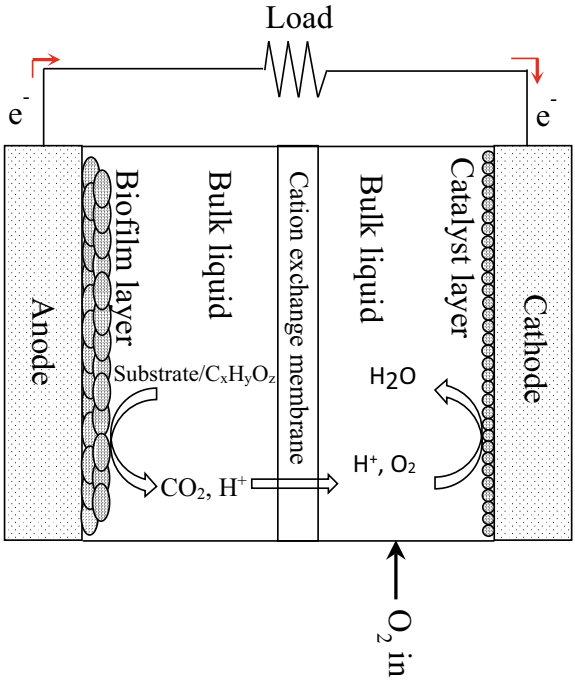

Fig. 1 Principle of microbial fuel cell based on proton transfer and oxygen reduction

1.1 Fundamentals of Electrogenesis in MFC

1.1.1 Maximum Voltages Defined by Thermodynamic Correlation

The achievable voltage from microbial fuel cells is typically in the range between 0.3 and 0.7 V. Voltage (E) is a product of external resistance (R_{ext}) and current (I), which is simply expressed as follows:

$$E = I R_{ext} \tag{1}$$

Given that the current produced in a single MFC (lab scale) is tiny, the current is estimated through the voltage drop across the resistor defined as $I = E/R$. The maximum achievable voltage generated by an MFC is the open-circuit voltage, or OCV, which can be quantified by disconnecting the circuit yielding zero current and infinite resistance. In this case, voltage drops as resistances are decreased. At any time, power is measurable using the following function:

$$P = E.I$$

Because of sluggish bacterial growth for biofilm formation on bioelectrode (bioanode), the voltage generation in MFC is more challenging to comprehend or anticipate than the voltage generated in a chemical fuel cell. Even voltage generated from a pure culture in MFC cannot be predicted, not to mention the voltage generated from a mixed culture. Relying on the thermodynamic relation between the substrate as electron donor and electron acceptor on the cathode, there are limits to the maximum achievable voltage in MFC.

To prove that statement, [19] learned an equation used for determining the maximum electromotive force (E_{emf}) in any type of battery or fuel cell and modified it to accommodate MFC systems which will be explained in detail in the next section. The original equation is given by

$$E_{emf} = E^o - \frac{RT}{nF}\ln(\Pi) \tag{2}$$

where E^o is the standard potential calculated from Gibbs free energy data provided by [44], $R = 8.31447$ J/mol K denotes the gas constant, T represents the absolute temperature (298 K), n signifies the number of transported electrons, F is Faraday's constant = 96,485 C/mol and Π is the ratio of [product] and [reactant] to the power of respective mol derived from the stoichiometric equation as shown below:

$$\Pi = \frac{[\text{products}]^p}{[\text{reactant}]^r} \tag{3}$$

The benefit of Eq. 2 is that it is positive for a favourable reaction and generates an E_{emf} value directly. This estimated E_{emf} establishes a ceiling for the cell voltage; the exact potential obtained through the empirical study of MFC is lower due to a variety of potential losses.

1.1.2 Theoretical Potential Based on Standard Electrode Potentials

Reactions that take place at the anode and cathode of MFC are classified as half-cell reactions. Under standard potential at 298 K, 1 M for liquid and 1 bar for gasses, the half-cell reaction is expressed in the form of scavenging electrons [1]. In the case of microbial acetate oxidation at the anode, the stoichiometric equation is as given below:

$$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O \tag{4}$$

Standard potentials determined in terms of the normal hydrogen electrode (NHE) under standard conditions have zero potential. Taking acetate oxidation for an example, considering $E^o = 0.187$ V, at pH 7, with reactant [HCO_3^-] and product [CH_3COO^-] concentration to be 5 mM and 16.9 mM, respectively, the theoretical potential of E_{An} is as indicated in Eqs. 5 and 6:

$$E_{An} = E_{An}^0 - \frac{RT}{8F}\ln\left(\frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9}\right) \tag{5}$$

$$E_{An} = 0.187 - \frac{(8.31 J/\text{molK})(298.15 K)}{(8)(9.65 \times 10^4 \text{C/mol})}\ln\frac{[0.0169]}{[0.005]^2[10^{-7}\text{M}]^9} = -0.300\text{V} \tag{6}$$

Under specific conditions, the theoretical anode potential (E_{An}) of different species with varied activities assuming equal concentration can be calculated by applying Eq. 2 (Table 1).

When oxygen is employed as the electron acceptor at the cathode, the half-cell reaction for oxygen reduction is

$$^1/_2\, O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{7}$$

Thus, the theoretical cathode potential for E_{Cat} is calculated by considering E^o (O_2) = 1.229 V and adjusted to pH = 7, as shown below:

$$E_{Cat} = E_{Cat}^o - \frac{RT}{nF} ln\left(\frac{1}{[O_2]^{1}/_2\,[H^+]^2}\right) \tag{8}$$

$$E_{Cat} = 1.229 - \frac{(8.31 J/molK)(298.15K)}{(2)(9.65\ x\ 10^4\ C/mol)} ln\frac{1}{[0.2]^{1}/_2\,[10^{-7}\ M]^2} = 0.\ 805\ V \tag{9}$$

Various catholyte have been utilised, generating different cell voltages. For instance, ferricyanide and manganese oxide have been employed as substitutes for oxygen. Over time, the pH of the catholyte might change, influencing the cathode potential. With the given standard potentials for various electron acceptors (catholyte) tabulated in Table 1 and plugged into Eq. 2, the theoretical cathode potential of different catholyte can be determined, which varied from 0.361 to 1.385 V. Thus, the E_{emf} of the MFC can be determined using the following equation:

$$E_{emf} = E_{Cat} - E_{An} \tag{10}$$

Assuming that oxygen is used as an electron acceptor at the cathode and acetate as an electron donor at the anode, under the set condition of 298 K, 1 bar and pH = 7, the resulted $E_{emf} = 0.805\ V - (-0.300\ V) = 1.105\ V$. Equation 10 shows that utilising similar anode compound in an MFC system with various catholyte parameters as given in Table 1 results in considerably varied cell voltages (E_{emf}), consequently, the power output levels. Different types of anode and cathode material would also affect the half-cell potential due to the magnitude of conductivity the material offers. The

Table 1 Reported standard anode and cathode potential (E_0) and respective theoretical potentials of MFC (E_{emf}) under specific conditions determined using Eq. 2. Both potentials are shown against the normal hydrogen electrode (NHE)

Reaction	E_o (V)	Conditions	E_{emf} (V)
Anode			
$2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$ [19]	1.23	$HCO_3^- = 5$ mM; $CH_3COO^- = 16.9$ mM; pH = 7	−0.300
		$HCO_3^- = 5$ mM; $CH_3COO^- = 5$ mM; pH = 7	−0.296
$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$ [35]	−0.014	pH = 7	−0.428
$CO_2 + HCO^-{}_3 + 8H^+ + 8e^- \rightarrow CH3COO^- + 3H_2O$ [35]	0.130	pH = 7	−0.284
Cathode			
$O_2^- + 4H^+ + 4e^- \rightarrow 2H_2O$ [19]	0.187	$pO_2 = 0.2$; mM; pH = 7	0.805
		$pO_2 = 0.2$; mM; pH = 10	0.627
$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ [19]	1.229	$[Mn^{2+}] = 5$ mM; pH = 7	0.470
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ [50]	1.70	$MnO_4^- = 10$ mM; pH 3.5	1.385
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ [19]	0.695	$pO_2 = 0.2$; $[H_2O_2] = 5$ mM; pH = 7	0.328
$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ [19]	0.361	$Fe(CN)_6^{3-} = Fe(CN)_6^{4-}$	0.361

amount of power generated by an MFC is consequently dependent on the catholyte selection; this should be considered when cross-comparison with the power densities generated from other MFCs in the literature.

1.2 Open Circuit Voltage (OCV) and Potential Losses

As explained earlier, the highest achievable potential of MFC is in the state of open-circuit voltage (OCV). OCV is measurable by disconnecting MFC from the circuit until no current flows across the circuit after a significant time. Removing the resistor should give MFC its OCV approaching the theoretical E_{emf} value of the cell. However, in most cases, the OCV is much lower than the E_{emf} value due to many possible reasons, indicating energy losses. In fact, E_{emf} is a thermodynamic parameter that does not take the internal resistance of cells into account. This energy loss is known as overpotential.

Knowing that the theoretical value of oxygen reduction at the cathode and pH 7 is 0.805 V, but because of the overpotential, the measured potential is typically around 0.2–0.3 V. The energy loss or overpotential value is simply determined by subtracting the theoretical and exact potential value (i.e., 0.805–0.2 V). In this case, 0.605 V has been lost, implying poor catalytic activity on the cathode, which demands the cell's catalytic improvement. One significant advantage of thermodynamic analysis through theoretical calculations is mainly to know how big and what type of energy losses are taking place in the cell.

2 Methods of Electron Transfer

2.1 Electron Shuttles or Mediators

Some microorganisms perform electron transfer with the aid of exogenous substances. Humic substances with quinone/hydroquinone groups are abundant in nature and act as electron acceptors for microbial respiration and oxidation of organic substrates, hydrogen and metals under anaerobic conditions [21, 39, 51]. Besides, they also act as electron donors for microbial respiration and reduce sulfides, nitrate and iron oxides [5, 27, 51]. Humic substances could also act as electron acceptors and donors; they are bacterially reduced along with microbial reductive dehalogenation of pentachlorophenol and iron oxides, which causes the humic substances to be re-oxidised [17]. The presence of humic substances accelerates electron transfer from bacteria to insoluble terminal electron acceptors [16]. They also facilitate the electron transfer of both in vivo and in vitro cytochrome C by promoting NADP generation [15, 43]. Apart from humic substances, iron-bearing minerals such as iron oxide and carbon-based conductive materials also promote electron transfer

by enhancing the connection of diverse microbial species. As electrons are loosely bound to their surfaces and are freely moving, they are widely employed as the electrode in a microbial fuel cell [47–49].

Anaerobic respiration of microorganisms produces small molecules as endogenous electron shuttles for interspecies electron transfer. Microorganisms synthesise primary metabolites such as H_2 and intermediary metabolites such as formate from oxidisable organic substrates such as ethanol, leaving the microbial cells in their reduced state to transfer electrons to distant extracellular oxidants interspecies electron transfer to its syntrophic partner. Ethanol is oxidised to acetate, and substrate-utilising bacteria or hydrogenotrophic bacteria liberate H_2. Syntrophic methanogenic bacteria then utilise H_2 to reduce carbon dioxide to methane [3, 9, 45]. The electron transfer by either H_2 or/and formate differs for different co-cultures as it relies on its syntrophic partner, either an H_2 using methanogen or a formate-utilising methanogen [9]. In microbial fuel cells, these metabolites can convey electrons towards iron oxides or electrodes [38].

Besides, bacteria also produce secondary metabolites such as phenazines and flavins as electron shuttles. Endogenous phenazine antibiotics such as pyocyanin and phenazine-1-carboxamide synthesised by *Pseudomonas aeruginosa* promote anaerobic survival of the bacteria through extracellular electron transfer [37]. The employment of phenazine antibiotics as electron transfer mediators enables the transfer of bacterial electrons towards the anode in a microbial fuel cell [12, 31, 32]. Flavins are another electron shuttling intermediate resulting from riboflavin's employment that promotes anoxic bacterial growth and accelerates the reduction of poorly crystalline Fe(III) oxide with fumarate as the sole electron acceptor [4, 6]. Flavins are also primary cytochrome-bound cofactors. However, its practicality in the microbial fuel cell is inconsistent due to its reliance on bacterial preference [22, 46].

2.2 C-Type Cytochromes

Cytochromes are distributed in the cytoplasm, inner membrane, periplasm and outer membrane, and some are secreted to the extracellular environment. Cytochromes with multiple iron porphyrins or hemes as prosthetic groups were found in diverse prokaryotes where they participated in electron transfer and biochemical cycling of N, S and Fe globally [2]. C-type cytochromes are the main cytochrome group with electron transfer importance. They can be found at the inner membrane (MacA), periplasmic (PpcA, PpcB, PpcC, PpcD and PpcE) and outer membrane (OmcF, OmcS, OmcE, OmcB and OmcZ) [24, 25, 36]. C-type cytochromes mainly accelerate electron transfer from microorganisms to insoluble electron acceptors by coupling with pili [14, 20, 41, 42]. OmcS facilitates electron transfer from pili to Fe(III) oxide, Mn(IV) oxide and humic substances rather than electron transfer along the pili filament [14, 20]. OmcZ promotes electron conductivity of microbial biofilm, whereas

OmcS and OmcE involve in electron transfer to electrodes [10, 11, 26]. Extracellular c-type cytochromes cause the reduction of Fe(III) oxide, Re(III), U(IV) and Cr(IV) due to the utilisation of these metals as terminal electron acceptors for anaerobic respiration [13, 18, 28, 40].

2.3 Nanowires

Microbial pili can act as "nanowires" to facilitate long-range respiration and conduct electrons between microbial cells and electron acceptors. They extend from the outer cell membrane of the microbial cell into the extracellular domain for long-distance extracellular electron transfer or conduction of electrons through biofilms [33, 34]. The electron acceptors can either be reducible substrates or syntrophic partners [20, 33]. There are two electron transfer mechanisms of microbial nanowires. Pili of *Shewanella oneidensis* are electrically conductive filaments that transfer electrons through electron hopping between cytochromes aligned along the filament of pili with inter-cytochrome spacing less than 0.7 nm [30]. In electron hopping, electrons are physically displaced due to diffusion and electron hop from a reduced cytochrome to its adjacent oxidised cytochrome [23]. On the other hand, pili of *Geobacter sulfurreducens* have metallic-like conductivity due to the overlapping of pi–pi orbitals of aromatic amino acids that result in electron delocalisation [8]. As a result, electrons are delocalised and spread across the entire filament of pili [7, 29]. Long-distance electron transfer via pili not only contributes to Fe(III) oxide reduction but is also crucial in interspecies electron exchange between syntrophic microbial partners [20].

3 Concluding Remarks

In MFC technology, obtaining the theoretically calculated potential and power is an endeavouring journey. Due to the added biological nature of the microorganism used, which is yet to be understood fully as to how the interaction between the abiotic and biotic components affects the MFC performance, one could only hope to approach the calculated values obtained through understanding the various equations and physics laws governing electrical generation. A fact to be reminded of is that there are a plethora of microorganisms available in the world, identified or not, with their own intrinsic nature. Thus, understanding how they interact with their surrounding environment could shed some clues and perhaps bring us closer to obtaining the theoretically calculated value. Therefore, there is an absolute must to further study these interactions to enhance knowledge in this field.

References

1. Bard AJ (2017) Standard potentials in aqueous solution. Routledge
2. Breuer M, Rosso KM, Blumberger J, Butt JN (2015) Multi-haem cytochromes in Shewanella oneidensis MR-1: structures, functions and opportunities. J R Soc Interface 12. https://doi.org/10.1098/rsif.2014.1117
3. Bryant MP, Wolin EA, Wolin MJ, Wolfe RS (1967) Methanobacillus omelianskii, a symbiotic association of two species of bacteria. Arch Mikrobiol 59:20–31
4. Chen S, Rotaru AE, Shrestha PM, et al (2014) Promoting interspecies electron transfer with biochar. Sci Rep 4. https://doi.org/10.1038/srep05019
5. Coates JD, Cole KA, Chakraborty R et al (2002) Diversity and ubiquity of bacteria capable of utilizing humic substances as electron donors for anaerobic respiration. Appl Environ Microbiol 68:2445–2452. https://doi.org/10.1128/AEM.68.5.2445-2452.2002
6. Edwards MJ, White GF, Norman M et al (2015) Redox linked Flavin sites in extracellular decaheme proteins involved in microbe-mineral electron transfer. Sci Rep 5:1–11. https://doi.org/10.1038/srep11677
7. Edwards PP, Gray HB, Lodge MTJ, Williams RJP (2008) Electron transfer and electronic conduction through an intervening medium. Angew Chem—Int Ed 47:6758–6765. https://doi.org/10.1002/anie.200703177
8. Giltner CL, Nguyen Y, Burrows LL (2012) Type IV Pilin proteins: versatile molecular modules. Microbiol Mol Biol Rev 76:740–772. https://doi.org/10.1128/mmbr.00035-12
9. Hattori S, Luo H, Shoun H, Kamagata Y (2001) Involvement of formate as an interspecies electron carrier in a syntrophic acetate-oxidizing anaerobic microorganism in coculture with methanogens. J Biosci Bioeng 91:294–298. https://doi.org/10.1016/S1389-1723(01)80137-7
10. Holmes DE, Chaudhuri SK, Nevin KP et al (2006) Microarray and genetic analysis of electron transfer to electrodes in Geobacter sulfurreducens. Environ Microbiol 8:1805–1815. https://doi.org/10.1111/j.1462-2920.2006.01065.x
11. Inoue K, Qian X, Morgado L et al (2010) Purification and characterization of OmcZ, an outer-surface, octaheme c-type cytochrome essential for optimal current production by geobacter sulfurreducens. Appl Environ Microbiol 76:3999–4007. https://doi.org/10.1128/AEM.00027-10
12. Jayapriya J, Ramamurthy V (2012) Use of non-native phenazines to improve the performance of Pseudomonas aeruginosa MTCC 2474 catalysed fuel cells. Bioresour Technol 124:23–28. https://doi.org/10.1016/j.biortech.2012.08.034
13. Kokhan O, Ponomarenko NS, Pokkuluri PR et al (2015) Bidirectional photoinduced electron transfer in ruthenium(II)-Tris-bipyridyl-Modified PpcA, a multi-heme c-type cytochrome from geobacter sulfurreducens. J Phys Chem B 119:7612–7624. https://doi.org/10.1021/jp511558f
14. Leang C, Qian X, Mester T, Lovley DR (2010) Alignment of the c-type cytochrome OmcS along pili of Geobacter sulfurreducens. Appl Environ Microbiol 76:4080–4084. https://doi.org/10.1128/AEM.00023-10
15. Li M, Su Y, Chen Y et al (2016) The effects of fulvic acid on microbial denitrification: promotion of NADH generation, electron transfer, and consumption. Appl Microbiol Biotechnol 100:5607–5618. https://doi.org/10.1007/s00253-016-7383-1
16. Li X, Liu L, Liu T et al (2013) Electron transfer capacity dependence of quinone-mediated Fe(III) reduction and current generation by Klebsiella pneumoniae L17. Chemosphere 92:218–224. https://doi.org/10.1016/j.chemosphere.2013.01.098
17. Liu G, Qiu S, Liu B et al (2017) Microbial reduction of Fe(III)-bearing clay minerals in the presence of humic acids. Sci Rep 7:1–9. https://doi.org/10.1038/srep45354
18. Liu T, Li X, Li F et al (2016) In situ spectral kinetics of Cr(VI) reduction by c-type cytochromes in A suspension of living shewanella putrefaciens 200. Sci Rep 6:1–11. https://doi.org/10.1038/srep29592
19. Logan BE, Hamelers B, Rozendal R et al (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40:5181–5192. https://doi.org/10.1021/es0605016

20. Lovley DR (2012) Long-range electron transport to Fe(III) oxide via pili with metallic-like conductivity. Biochem Soc Trans 40:1186–1190. https://doi.org/10.1042/BST20120131
21. Lovley DR, Coates JD, Blunt-Harris EL et al (1996) Humic substances as electron acceptors for microbial respiration. Nature 382:445–448
22. Masuda M, Freguia S, Wang YF et al (2010) Flavins contained in yeast extract are exploited for anodic electron transfer by Lactococcus lactis. Bioelectrochemistry 78:173–175. https://doi.org/10.1016/j.bioelechem.2009.08.004
23. McCreery RL (2004) Molecular electronic junctions. Chem Mater 16:4477–4496. https://doi.org/10.1021/cm049517q
24. McKenzie AM (2016) Ultrafast limits of photo-induced electron transfer rates in PPCA, a multi-heme C-type cytochrome. Biophys J 110:18a. https://doi.org/10.1016/j.bpj.2015.11.156
25. Mehta T, Coppi MV, Childers SE, Lovley DR (2005) Outer membrane c-type cytochromes required for Fe(III) and Mn(IV) oxide reduction in Geobacter sulfurreducens. Appl Environ Microbiol 71:8634–8641. https://doi.org/10.1128/AEM.71.12.8634-8641.2005
26. Nevin KP, Kim BC, Glaven RH, et al (2009) Anode biofilm transcriptomics reveals outer surface components essential for high density current production in Geobacter sulfurreducens fuel cells. PLoS One 4. https://doi.org/10.1371/journal.pone.0005628
27. Orsetti S, Laskov C, Haderlein SB (2013) Electron transfer between iron minerals and quinones: estimating the reduction potential of the Fe(II)-goethite surface from AQDS speciation. Environ Sci Technol 47:14161–14168. https://doi.org/10.1021/es403658g
28. Paquete CM, Fonseca BM, Cruz DR et al (2014) Exploring the molecular mechanisms of electron shuttling across the microbe/metal space. Front Microbiol 5:1–12. https://doi.org/10.3389/fmicb.2014.00318
29. Petty MC (2007) Molecular electronics: from principles to practice. Mol Electron From Princ Pract 1–521. https://doi.org/10.1002/9780470723890
30. Pirbadian S, El-Naggar MY (2012) Multistep hopping and extracellular charge transfer in microbial redox chains. Phys Chem Chem Phys 14:13802–13808. https://doi.org/10.1039/c2cp41185g
31. Rabaey K, Boon N, Höfte M, Verstraete W (2005) Microbial phenazine production enhances electron transfer in biofuel cells. Environ Sci Technol 39:3401–3408. https://doi.org/10.1021/es048563o
32. Rabaey K, Boon N, Siciliano SD et al (2004) Biofuel cells select for microbial consortia that self-mediate electron transfer. Appl Environ Microbiol 70:5373–5382. https://doi.org/10.1128/AEM.70.9.5373
33. Reguera G (2015) Microbes, cables, and an electrical touch. Int Microbiol 18:151–157. https://doi.org/10.2436/20.1501.01.245
34. Richter LV, Franks AE, Weis RM, Sandler SJ (2017) Significance of a posttranslational modification of the PilA protein of Geobacter sulfurreducens for surface attachment, biofilm formation, and growth on insoluble extracellular electron acceptors. J Bacteriol 199. https://doi.org/10.1128/JB.00716-16
35. Rittmann BE, McCarty PL (2001) Environmental biotechnology: principles and applications. McGraw-Hill Education
36. Santos TC, Silva MA, Morgado L et al (2015) Diving into the redox properties of Geobacter sulfurreducens cytochromes: a model for extracellular electron transfer. Dalt Trans 44:9335–9344. https://doi.org/10.1039/c5dt00556f
37. Schmitz S, Nies S, Wierckx N et al (2015) Engineering mediator-based electroactivity in the obligate aerobic bacterium Pseudomonas putida KT2440. Front Microbiol 6:1–13. https://doi.org/10.3389/fmicb.2015.00284
38. Schröder U, Nießen J, Scholz F (2003) A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude. Angew Chem 115:2986–2989. https://doi.org/10.1002/ange.200350918
39. Scott DT, Mcknight DM, Blunt-Harris EL et al (1998) Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms. Environ Sci Technol 32:2984–2989. https://doi.org/10.1021/es980272q

40. Shelobolina ES, Coppi MV, Korenevsky AA et al (2007) Importance of c-type cytochromes for U(VI) reduction by Geobacter sulfurreducens. BMC Microbiol 7:1–15. https://doi.org/10.1186/1471-2180-7-16
41. Shrestha PM, Rotaru AE, Summers ZM et al (2013) Transcriptomic and genetic analysis of direct interspecies electron transfer. Appl Environ Microbiol 79:2397–2404. https://doi.org/10.1128/AEM.03837-12
42. Strycharz SM, Glaven RH, Coppi MV et al (2011) Gene expression and deletion analysis of mechanisms for electron transfer from electrodes to Geobacter sulfurreducens. Bioelectrochemistry 80:142–150. https://doi.org/10.1016/j.bioelechem.2010.07.005
43. Tang J, Liu Y, Yuan Y, Zhou S (2014) Humic acid-enhanced electron transfer of in vivo cytochrome c as revealed by electrochemical and spectroscopic approaches. J Environ Sci (China) 26:1118–1124. https://doi.org/10.1016/S1001-0742(13)60518-5
44. Thauer RK, Jungermann K, Decker K (1977) Energy conservation in chemotrophic anaerobic bacteria. Bacteriol Rev 41:100–180. https://doi.org/10.1128/mmbr.41.1.100-180.1977
45. Thiele JH, Zeikus JG (1988) Control of interspecies electron flow during anaerobic digestion: significance of formate transfer versus hydrogen transfer during syntrophic methanogenesis in flocs. Appl Environ Microbiol 54:20–29. https://doi.org/10.1128/aem.54.1.20-29.1988
46. Xu S, Jangir Y, El-Naggar MY (2016) Disentangling the roles of free and cytochrome-bound flavins in extracellular electron transport from Shewanella oneidensis MR-1. Electrochim Acta 198:49–55. https://doi.org/10.1016/j.electacta.2016.03.074
47. Yin Q, Hu Z, Sun Y et al (2017) Effect of the dosage of ferroferric oxide on batch anaerobic treatment of high strength synthetic wastewater. Desalin Water Treat 91:152–158. https://doi.org/10.5004/dwt.2017.20737
48. Yin Q, Miao J, Li B, Wu G (2017b) Enhancing electron transfer by ferroferric oxide during the anaerobic treatment of synthetic wastewater with mixed organic carbon. Int Biodeterior Biodegrad 119:104–110. https://doi.org/10.1016/j.ibiod.2016.09.023
49. You S, Ma M, Wang W, et al (2017) 3D Macroporous nitrogen-enriched graphitic carbon scaffold for efficient bioelectricity generation in microbial fuel cells. Adv Energy Mater 7. https://doi.org/10.1002/aenm.201601364
50. You S, Zhao Q, Zhang J et al (2006) A microbial fuel cell using permanganate as the cathodic electron acceptor. J Power Sour 162:1409–1415. https://doi.org/10.1016/j.jpowsour.2006.07.063
51. Yu ZG, Orsetti S, Haderlein SB, Knorr KH (2016) Electron transfer between sulfide and humic acid: electrochemical evaluation of the reactivity of sigma-aldrich humic acid toward sulfide. Aquat Geochem 22:117–130. https://doi.org/10.1007/s10498-015-9280-0

Design and Configuration of Microbial Fuel Cells

Tooba Touqeer, Waheed Miran, Muhammad Waseem Mumtaz, and Hamid Mukhtar

Abstract The use of bacterial metabolism to oxidize organic matter and transfer electrons to the solid surface (electrode) leads to the development of microbial fuel cell (MFC) technology. Although MFCs have been utilized for biosensors, metals ion recovery, nutrient remediations, and synthesis of organic compounds; however, wastewater treatment and bioelectricity generation is the most generic application of MFC technology. The limitation in the commercialization of MFC is the lower power output and lack of efficient scale-ups. The MFC performance has been improved by optimizing the process parameters and various MFC reactor configurations with a focus on optimizing ohmic resistance, mass transport, and reaction kinetics. The vast research carried out on MFCs globally has led to various reactor designs. The vital components of MFC design include a group of separators, electrode materials, and reactor geometry. This chapter gives a detailed overview of conventional MFC configurations and current development in the innovative MFC designs for enhanced MFC performance and novel applications.

Keywords Microbial fuel cell · Scale-up · High-throughput system · Wastewater treatment · Bioelectricity

1 Introduction

Organic wastes and wastewater treatment are necessary for environmental protection that requires high energy [41]. Also, rapidly depleting fossil fuel resources

T. Touqeer · M. W. Mumtaz (✉)
Department of Chemistry, University of Gujrat, Gujrat 50700, Punjab, Pakistan
e-mail: muhammad.waseem@uog.edu.pk

W. Miran (✉)
School of Chemical and Materials Engineering, National University of Sciences and Technology, Islamabad 44000, Pakistan
e-mail: waheed.miran@scme.nust.edu.pk

H. Mukhtar
Institute of Industrial Biotechnology, Government College University Lahore, Lahore, Pakistan

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_3

along with a recent increase in their consumption are serious global issues [49]. These problems have urged scientists globally to find renewable energy resources and economical waste treatment technologies [64]. In this regard, the use of microorganisms to produce electricity with subsequent waste treatment has emerged as a potential technology termed microbial fuel cell (MFC) [58]. In MFC, the microorganisms act as biocatalysts and help in degrading the wastes which are ultimately converted into biocurrent/bioelectricity. This eco-friendly electrochemical device provides dual benefits, i.e., waste treatment and electricity generation [40]. MFCs have been employed for various kinds of municipal as well as industrial wastewaters for simultaneous electricity generation and wastewater treatment [16, 38]. Other applications include biosensors, metal ion recovery, nutrient remediations, and the synthesis of high-value compounds.

Generally, the MFC comprises cathode and anode chambers which are separated by a proton exchange membrane (PEM) [29]. The anodic chamber contains microbes that act as a biocatalyst to decompose waste materials. As a result, electrons are produced that are transferred to the cathodic chamber via an external circuit. The protons diffuse to the cathode through PEM and combine with electrons and O_2 to form water [15]. In most of the cases, current production is very small, so many advancements have been suggested by the scientists to get better performance by the MFCs and to find the most suitable feedstock [2], microbial consortia [26], catholyte/anolyte strength [34], and electrodes [44]. Electrochemical cell configuration is another very important domain that could improve the MFC performance [65].

The commercialization of MFCs requires the scaling-up of reactors. Various proposals which have been suggested include modifications in the design of electrodes, the design of membrane, using membrane-less reactors, and stacked systems. Some researchers have shown that a linear increase in power output can be achieved by expanding the size of MFC systems by stacking many units [69]. To get better power output, many researchers recommend minimizing the size of the MFCs system and sustaining a high feedstock supply, with optimization of the number of units for efficient performance. Another advantage of minimizing the MFC size is to explore MFC for various micro-level applications such as remote biosensors instead of bioenergy generation (which aims at offsetting the power requirements for wastewater treatment). In recent times, high-throughput MFC systems have been also designed for expediting the research in the MFC field by studying many parameters simultaneously for optimizing the MFC systems. In this chapter, we will discuss the advancements in configuration and design of MFCs which are economically feasible and that could be utilized to scale up the MFC reactor to get improved outputs. Future aspects and suggestions to further advance the MFC technology are also discussed.

2 Design and Configuration of MFCs Reactor

Cell design is a very important component in the successful operation of MFC. There is not a single standard size, configuration, or design for the MFC reactors. The configuration is entirely dependent on the researchers for a specific application. MFC performance based on reactors configuration could be controlled by various factors such as varying volumes, supply of oxygen, area of the membrane, and spacing of electrode [39]. Different reactor shapes, such as cylindrical, cubic, horseshoe, and H-shaped reactors have been proposed. Single and dual-chamber MFC reactors have been commonly studied in most MFC research projects [51]. Among the various shapes of MFC, H-shaped reactors are typically used in MFC due to the easy placement of PEM. The cell material could be glass or some type of plastic [20]. The size of the reactor varies from square centimeters to square meters having a volume of microliters to thousand liters [8]. MFC configurations based on different designs are discussed below.

2.1 Configuration Based on Number of MFC Chambers

2.1.1 Single-Chamber MFCs

Natural aeration of cathode for utilizing O_2 as the ultimate electron acceptor leads to the construction of MFCs with one chamber and air cathode assembly (Fig. 1). In the single-chamber MFCs, the cathode is directly connected to PEM permitting a direct supply of oxygen to the electrode [67]. Several advantages associated with single-chamber MFC include simple operation, less internal resistance, small electrode spacing, better proton diffusion as well as an efficient cathode for O_2 reduction [70]. Since no aeration is provided by using a compressor/pump and also catholyte is not required, this configuration makes it more easily adaptable and less expensive. In addition, more power density of single-chamber cell as compared to dual-chamber MFC has been reported in earlier studies [37]. Mainly this type of configuration

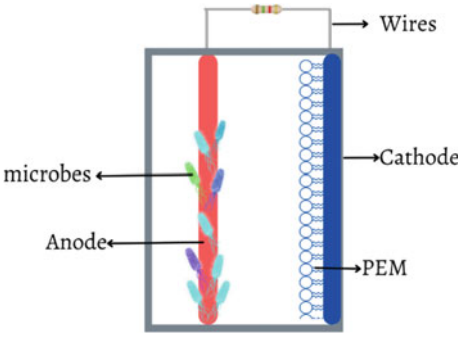

Fig. 1 Schematic presentation of a single-chamber MFC

comprises simple anodic chambers with no distinctive cathodic chamber and sometimes without any PEM. Cathode having pores on a side of the wall utilizes atmospheric oxygen and permits the protons to diffuse through the pores. The single-cell configuration is attracting researchers because of the above-mentioned advantages as well as ease of scaling-up of the system as compared to the dual-chamber MFCs [6, 37]. Carbon electrodes are used as anode in single-chamber MFC while the cathode is mostly PEM/carbon cloth hybrid or porous carbon electrodes [51]. However, cathode might be enclosed in graphite where electrolytes are added slowly which act as catholyte and avoided drying of the cathode and its membrane. Hence, fluid management is a limiting factor in such constructed cells. On the other hand, leakage of fluid, diffusion of oxygen, and evaporation are the flaws of this configuration and need to be addressed for efficient MFCs' operation. The use of different diffusion layers on the cathode surface has been proved to get better power density and oxygen diffusion [5, 71]. A comparison of a few of the studies involving single-chamber MFCs has been reported in Table 1.

2.1.2 Dual-Chamber MFCs

The two or dual-chambered MFC is also commonly used for energy generation along with wastewater treatment. It comprises anodic and cathodic compartments separated via a PEM (Fig. 2). PEM functions as a medium for the transfer of protons from the anode compartment to the cathode compartment [27]. The PEM also helps to prevent diffusion/contact of oxygen and other oxidizing agents to the anode [35].

Table 1 A comparison of single-chamber MFCs

Anode materials	Substrate	Power density	Coulombic efficiency	Microbial community	References
Graphite electrodes	Domestic wastewater	26 mW/m^2	-	*Geobacter metallireducens*	Liu et al. [36]
Carbon cloth	Artificial wastewater	-	5%	Activated sludge	Di Lorenzo et al. [12]
Toray carbon paper	Domestic wastewater	28 mW/m^2	28%	Bacteria from domestic wastewater	Liu and Logan [35]
Graphite pellets	Artificial wastewater	1.3 W/m^3	68%	Sludge collected from the treatment plant	Di Lorenzo et al. [13]
Carbon cloth	Beer brewery wastewater	483 mW/m^2 (12 W/m^3)	38%	Bacteria from domestic wastewater	Wang et al. [66]
Graphite coated stainless steel mesh	Dairy wastewater	20.2 W/m^3	26.87%	Mixed culture collected from dairy wastewater treatment plant	Mardanpour et al. [42]

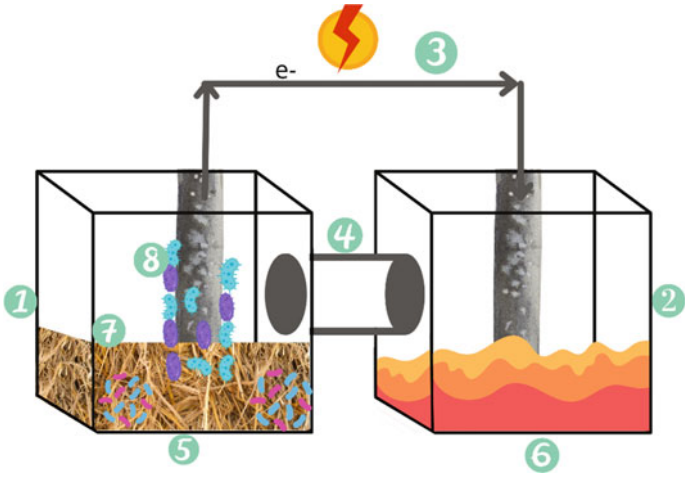

Fig. 2 Main components of dual-chamber MFC: 1. Anodic chamber with anaerobic conditions; 2. Cathodic chamber with air supply; 3. Wire for connecting electrodes; 4. Proton exchange membrane (PEM)/salt bridge; 5. Substrate to feed bacteria; 6. Catholyte; 7. Bacterial culture, and 8. Anode (with bacterial attachments)

Some problems associated with the dual-chamber microbial fuel cell are the large distance between the electrodes, which causes more internal resistance, the use of a batch process which requires regular maintenance, and enrichment of medium by some additives to get high current generation [52, 72]. These conditions for optimum power production are the hindrance to scaling up of the dual-chamber MFCs. Many studies have focused on the advancement of dual-chamber MFC to overcome the above-mentioned problems. For example, the internal resistance has been tried to reduce by having fewer distances between the two electrodes and placing them closer to the PEM but this will eventually reduce the power density by having more diffusion of O_2 from the cathodic chamber to the anodic side [18]. The continuous mode MFC has also been proposed which provides even better power density than simple bottle types dual-chamber MFC. In continuous mode dual-chamber MFC, configuration comprised a cathode hot pressed on a PEM connected with the anode and anchored with two polycarbonate plates where both chambers can be fed with feedstock in a continuous manner. Changing the electrode material in dual-chamber MFCs has also been shown to gain high MFC performance without the use of any external additives [30, 59]. Various other designs of two-chamber MFCs have also been proposed to resolve the issues related to the lower current output.

2.1.3 Stacked MFCs

Since scaled-up MFCs are urgently required to commercialize the MFC technology, stacking arrangements of modular multiple units is an applicable solution while

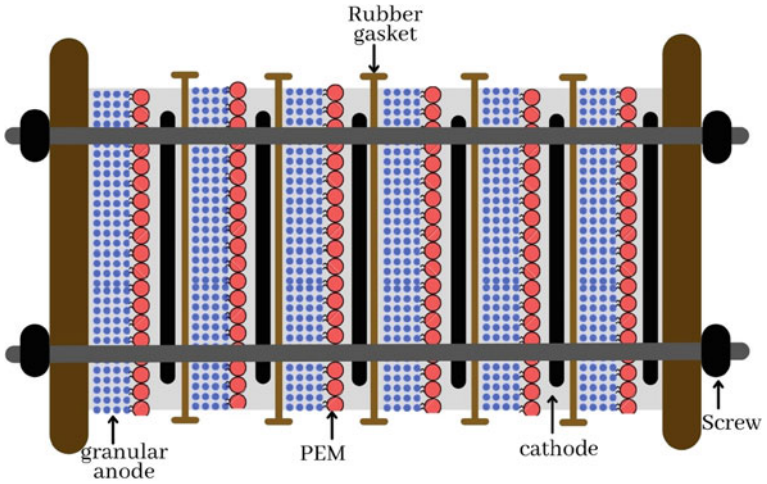

Fig. 3 Schematic presentation of stacked MFC

utilizing advanced power management systems [25]. In real applications, the multi-electrode assembly from the modular designs coupled with an electrical circuit for the storage of charge has been proposed for stacked MFCs [24]. A battery-style MFC can be formed by stacking the fuel cells (Fig. 3). The cell efficacy, i.e., power density, current, and voltage is known to be improved in stacked cells. Moreover, the Columbic efficacy of individual cell also remains unaffected. The cell stacking may be in a series or parallel manner [14]. Both methods are important and could be utilized as conventional power sources and the voltage and current requirements of electronic devices could be achieved. The design of parallel or series stacked MFC circuits is very crucial, and shape modulation and horizontal and vertical directions of the staking can considerably affect the cell efficacy [43, 57]. Efforts are in progress to further improve the MFC technology with better efficiency and feasibility, and for utilizing MFC stacks to meet the practical needs of the industry and society.

2.1.4 Configuration Based on MFC Size

MFC size is another design parameter intensively studied for commercializing the MFC technology. In this regard microliter to thousands of liter-scale MFC have been studied for various applications. The small-scale MFC manufacturing and deployment are relatively easy. In addition, they offer better prospects as a long-standing power source at distant sites for the avoidance of regular maintenance, converting waste into electricity and non-requirement of refined chemicals [4, 46]. Liter-sized MFCs have also been used for process optimizations and the development of MFC technology for practical purposes [3, 32]. Nevertheless, small-sized cells present better efficiency because of the small electrode distance which helps to avoid internal

resistance. Another advantage is the small-sized electrode present provides a high surface-to-volume ratio and fast response time. Furthermore, the surface modification of small-sized electrode is far easier and more economical, and it offers better performance than large size cells [19]. Generic techniques for MFC fabrication are etching, metal deposition photolithography, and polymer molding. These could be applied for the fabrication of micro as well as macro-sized cells. Although large size MFCs provide better electrode material and microbial performance assessment, the conventional large-sized MFCs have limited performance because of large resistance and the low surface-to-volume ratio [11, 22]. High-throughput MFC systems are another domain in which investigations are being carried out for the advancement of the MFC system. Keeping in view the importance of micro-sized and high-throughput MFC systems, further discussion is provided below.

2.1.5 Micro-sized MFCs

The milliliter-scale MFCs have a huge potential for long-term power supply at remote sites where a regular change of batteries is impractical. The capability of bacteria for producing bioelectricity using indigenous resources helps in the easy deployment of micro-sized MFCs as there is no requirement for an external power source and artificial mediators [55]. With a proper supply of the carbon source, microbes' propagation and replenishing enable self-sustainable power generation. Other than milliliter-scale MFCs representation of miniatured MFCs, such MFCs are also designed for on-chip power production and fast screening of optimum operating conditions. The micro-sized MFC offers very unique features, such as a large surface area-to-volume ratio, shorter electrode distance, faster response time, and lower Reynolds number, along with various choices of design in constructing MFCs. The fabrications of miniature MFC devices are known to have high precision and have less cost when microfabrication processes are utilized. Also, the materials utilized for fabricating this type of MFCs are usually of inert character and have suitability for microbial research. The miniatured MFCs having carbon-based anodes [56] or improved designs having cloth electrode shows high efficiency than large-scale MFCs in terms of volumetric current and power densities [68]. The current milliliter-scale MFCs still have an issue of lower volumetric power densities and coulombic efficiencies because of the higher internal resistance. Nevertheless, such MFC systems have huge potential in the fast screening of electrochemically active strains and electrode materials [23].

Current microfabrication techniques offer improved design of MFCs having submicroliter reactor volume that enables improved biofilm growth at anodic electrode [53] and a quick startup [10]. Most of the miniatured MFC devices used similar design configurations as of the conventional dual-chamber MFC, i.e., they have anodic and cathodic chambers parted by a PEM. Polydimethylsiloxane (PDMS) and silicon are extensively utilized in such MFCs owing to the flexible designs they offer in microfabrication. Because of the smaller reactor volume, miniatured MFCs are usually provided with the electrolyte replenishing system for continuous or periodic exchange, and hence allow sustained operations [9, 54]. For instance, Fig. 4a

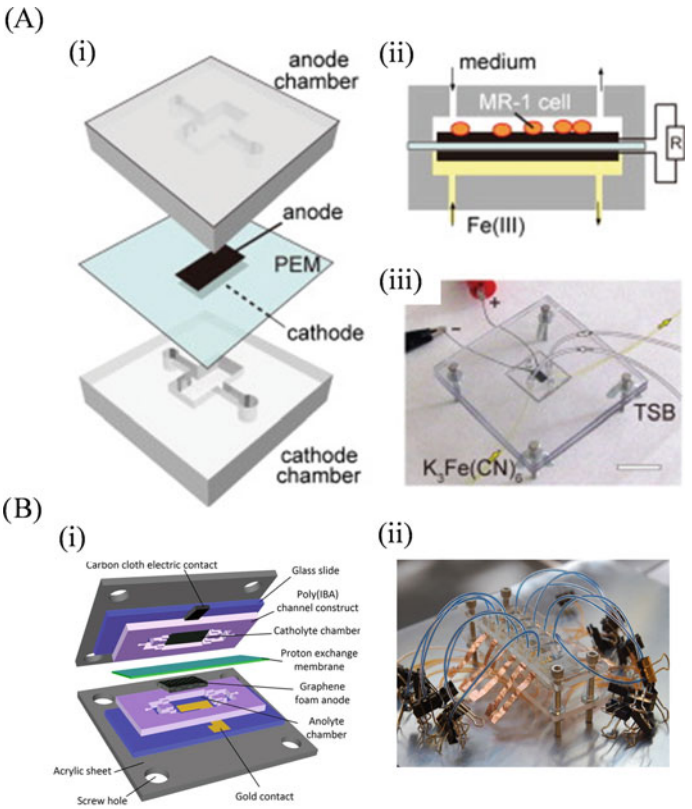

Fig. 4 **A** The design and assembly of a micro-MFC (i) the single MFC parts, (ii) a cross-sectional view of the MFC, and (iii) a picture of a PDMS micro-MFC. The scale bar is 2 cm. Adopted from [54]. **B** Microfluidic MFC design, showing (i) schematic of the device parts for the microfluidic MFC. (ii) Photograph of a ~1 × 1 × 3 $inch^3$ array of six microfluidic MFCs. Adopted from [28]

shows a micro-sized MFC system with a 4 μl chambers volume that has microfluidic flow cells for both anodes and cathodes [54]. Reproducible bioelectricity production and improved power densities were established. Further micro-sized improved MFC designs (Fig. 4b) allow the sustaining of a higher level of nutrient utilization, minimized the consumption of substrates, and reduced the response time of bioelectricity generation because of the fast mass transport [28].

Yet there are shortcomings in such MFC systems and to resolve these issues such as lower power of miniaturized MFCs, a combination of multiple MFCs in series or parallel can be utilized which help in achieving larger current and power output. Also, there is a reversal of voltage issue in these network systems which is required to be resolved for the long-term operation of MFC-based sensor networks and/or environmental toxin monitoring systems. A comparison of different micro-sized MFCs is provided in Table 2.

Table 2 A comparison of micro-scaled MFCs

Cell material	Microbes	Volume of anodic chamber	Anode material	Electrode distance	Power density	Columbic efficiency (%)	Refs.
Silicon	*Saccharomyces cevevisiae*	16 μL	Gold	160 μm	0.5 W/m^3	0.027	Chiao et al. [7]
Gortex	*Shewanella purtrefaciens*	10 μL	Gold with SAM	100 μm	–	–	Crittenden et al. [10]
PDMS/silicon	*Shewanella oneidensis* MR-1	1.5 μL	Gold	100 μm	15.3 W/m^3	2.8	Qian et al. [53]
Plastic	*Shewanella oneidensis* DSP-10	1.2 ml	Graphite felt	175 μm	660 W/m^3	8.3	Ringeisen et al. [56]
Plastic	Mixed bacterial culture	2.5 ml	Carbon cloth	1.7 cm	1010 W/m^3	71	Fan et al. [17]

2.1.6 High-Throughput MFCs

High-throughput MFCs are recently developed and used for the evaluation and microbial enrichment in different process conditions. In recent times [48], a 128-channel potentiostat is developed that connects with the printed circuit board. The entire array of channels was dipped in the anolyte medium, while a common reference electrode was used to carry out a high-throughput investigation for checking the effects of anode potentials on electroactive bacterial biofilms (Fig. 5a). Earlier, Zhou et al. developed a well-plate high-throughput colorimetry-based assay for the monitoring of bacterial respiration, which can show the presence of electroactive microbes associated with extracellular electron transfer (EET) capability [73]. Also, paper-based electrofluidic arrays having 6, 8, 64, and 96 wells via the fabrication method of wax printing have also been developed [21, 62, 63]. These designs help in eliminating the issues of small MFC devices such as large internal resistance, complicated assembling, and lower sample accessibility. One of the high-throughput-developed MFC reactors having 96-well plate showed these characteristics as well [60]. Additionally, it enables longer operational capability and reusability which helps in selective enrichments of EET-capable microbial culture. Also, such designs have better strength; therefore, they can be used for fieldwork which enables high-throughput in situ operations. The well plate connected to the potentiostat by electrical connections was similar to that described earlier [47]. Since the most widely studied application of MFCs is wastewater treatment, the microbial culture needs to be enriched for the specific wastewater treatment and to improve MFC performance. In this regard, preconditioning of consortia can be done using high-throughput systems which can help in achieving an easy scale-up process [1, 31]. For instance, a new 96-well MFC developed array (Fig. 5b) helped in the screening, selection, and sources of enriched EET culture by high-throughput [61]. The high-throughput MFC systems are still in their infancy, and continuous efforts are in progress to make them more reliable and useful for screening various optimization parameters.

3 Conclusions and Future Prospects

Various designs and configurations have been developed for MFCs to improve their performance and achieve commercialization of this emerging biotechnology. The designs and configurations include single chamber, dual chamber, stacked, microsized, large scale, and high throughput MFC systems. There is significant progress in the MFC research owing to various designs; however, many commercialization challenges are still being addressed and need further research. In addition to improving the power densities under real conditions, the capital and running costs linked with materials such as electrodes must be further reduced. For this, costly anodic and cathodic electrodes and catalyst layers on the cathode should not be used, as these costs add largely to the cost of MFC construction. Further scaling up is required with high surface area anodes and cathodes, which can help in achieving larger power

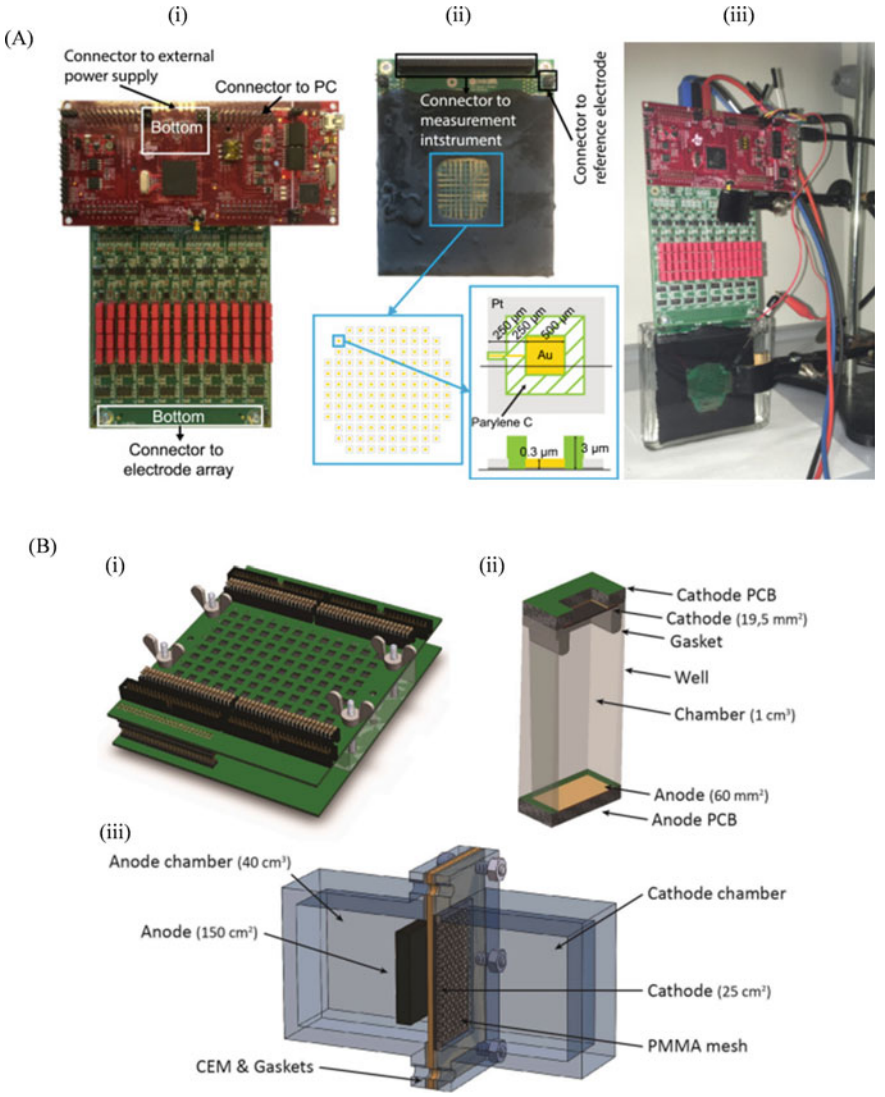

Fig. 5 **A** High-throughput bioelectrochemical system (i) a potentiostat having 128 channels connected to the computer (top view), (ii) 128 gold WE (0.5×0.5 mm^2) and platinum CE's scheme, and (iii) a complete bioelectrochemical system having 128-electrode array which is immersed in an electrolyte having a single RE. Adopted from [48]. **B** 3-D view of a 96-well MFC system including (i) the complete plate, (ii) cross-sections of individual wells, and (iii) a schematic of large-scale MFC. Adopted from [61].

densities. In the current scenario, because of lower bioelectricity production, expensive materials, and the continuously decreasing cost of renewable energy, it is less likely that bioelectricity produced from MFCs will outplay existing technologies. Therefore, applications other than bioelectricity production should also be considered and explored. Further, research is required in exploring the device configurations for minimizing the internal resistances for the improvement of micro-sized MFCs. Similarly, the high-throughput MFC systems for studying the impact of electrode's potential and external load for controlling bacterial metabolism are vital for understanding MFC operations. Currently, there are limited studies about high throughput MFC systems for EET capable microbial species and communities and it has huge potential for making a breakthrough in the commercialization of MFC technology. High throughput MFCs can be effectively utilized for various applications such as genetic engineering, screening of phenotypes, and mutants development studies for both microbial communities and single cultures [61]. With the recent discovery of human pathogens having EET capability [35, 45, 50], these systems can be very useful for evaluating the current production mechanism and the importance of EET-capable pathogens in human health, which can open a spectrum of new research areas.

References

1. AlSayed A, Soliman M, Eldyasti A (2020) Microbial fuel cells for municipal wastewater treatment: from technology fundamentals to full-scale development. Renew Sustain Energy Rev 134:110367
2. Angosto J, Fernández-López J, Godínez C (2015) Brewery and liquid manure wastewaters as potential feedstocks for microbial fuel cells: a performance study. Environ Technol 36(1):68–78
3. Babanova S, Jones J, Phadke S, Lu M, Angulo C, Garcia J, Carpenter K, Cortese R, Chen S, Phan T, Bretschger O (2020) Continuous flow, large-scale, microbial fuel cell system for the sustained treatment of swine waste. Water Environ Res 92(1):60–72. https://doi.org/10.1002/wer.1183
4. Chen S, Patil SA, Brown RK, Schröder U (2019) Strategies for optimizing the power output of microbial fuel cells: transitioning from fundamental studies to practical implementation. Appl Energy 233:15–28
5. Cheng S, Liu H, Logan BE (2006) Increased performance of single-chamber microbial fuel cells using an improved cathode structure. Electrochem Commun 8(3):489–494
6. Cheng S, Logan BE (2011) Increasing power generation for scaling up single-chamber air cathode microbial fuel cells. Biores Technol 102(6):4468–4473. https://doi.org/10.1016/j.biortech.2010.12.104
7. Chiao M, Lam KB, Lin L (2006) Micromachined microbial and photosynthetic fuel cells. J Micromech Microeng 16(12):2547
8. Choi S, Chae J (2013) Optimal biofilm formation and power generation in a micro-sized microbial fuel cell (MFC). Sens Actuat A 195:206–212
9. Choi S, Lee H-S, Yang Y, Parameswaran P, Torres CI, Rittmann BE, Chae J (2011) A μL-scale micromachined microbial fuel cell having high power density. Lab Chip 11(6):1110–1117. https://doi.org/10.1039/C0LC00494D
10. Crittenden SR, Sund CJ, Sumner JJ (2006) Mediating electron transfer from bacteria to a gold electrode via a self-assembled monolayer. Langmuir 22(23):9473–9476

11. Dewan A, Beyenal H, Lewandowski Z (2008) Scaling up microbial fuel cells. Environ Sci Technol 42(20):7643–7648
12. Di Lorenzo M, Curtis TP, Head IM, Scott K (2009) A single-chamber microbial fuel cell as a biosensor for wastewaters. Water Res 43(13):3145–3154
13. Di Lorenzo M, Scott K, Curtis TP, Head IM (2010) Effect of increasing anode surface area on the performance of a single chamber microbial fuel cell. Chem Eng J 156(1):40–48
14. Dizhou L, Meiying X, Yonggang Y (2020) Research progress of series and parallel stack of microbial fuel cells. Environ Chem 8:2227–2236
15. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25(5):464–482
16. Fadzli FS, Bhawani SA, Adam Mohammad RE (2021) Microbial fuel cell: recent developments in organic substrate use and bacterial electrode interaction. J Chem 2021
17. Fan Y, Hu H, Liu H (2007) Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. J Power Sour 171(2):348–354
18. Fan Y, Sharbrough E, Liu H (2008) Quantification of the internal resistance distribution of microbial fuel cells. Environ Sci Technol 42(21):8101–8107
19. Feng Y, He W, Liu J, Wang X, Qu Y, Ren N (2014) A horizontal plug flow and stackable pilot microbial fuel cell for municipal wastewater treatment. Biores Technol 156:132–138
20. Flimban SG, Ismail IM, Kim T, Oh S-E (2019) Overview of recent advancements in the microbial fuel cell from fundamentals to applications: design, major elements, and scalability. Energies 12(17):3390
21. Gao Y, Hassett DJ, Choi S (2017) Rapid characterization of bacterial electrogenicity using a single-sheet paper-based electrofluidic array. Front Bioeng Biotechnol 5:44. https://doi.org/10.3389/fbioe.2017.00044
22. Hiegemann H, Littfinski T, Krimmler S, Lübken M, Klein D, Schmelz K-G, Ooms K, Pant D, Wichern M (2019) Performance and inorganic fouling of a submergible 255 L prototype microbial fuel cell module during continuous long-term operation with real municipal wastewater under practical conditions. Bioresour Technol 294:122227
23. Hou H, Li L, Cho Y, de Figueiredo P, Han A (2009) Microfabricated microbial fuel cell arrays reveal electrochemically active microbes. PLoS ONE 4(8):e6570–e6570. https://doi.org/10.1371/journal.pone.0006570
24. Ieropoulos I, Greenman J, Melhuish C (2008) Microbial fuel cells based on carbon veil electrodes: stack configuration and scalability. Int J Energy Res 32(13):1228–1240. https://doi.org/10.1002/er.1419
25. Jadhav D, Mungray AK, Arkatkar A, Kumar S (2021) Recent advancement in scaling-up applications of microbial fuel cells: from reality to practicability. Sustain Energy Technol Assess 45:101226. https://doi.org/10.1016/j.seta.2021.101226
26. Jadhav DA, Ghangrekar MM (2020) Optimising the proportion of pure and mixed culture in inoculum to enhance the performance of microbial fuel cells. Int J Environ Technol Manag 23(1):50–67
27. Jia Q, Wei L, Han H, Shen J (2014) Factors that influence the performance of two-chamber microbial fuel cell. Int J Hydrogen Energy 39(25):13687–13693
28. Jiang H, Ali MA, Xu Z, Halverson LJ, Dong L (2017) Integrated microfluidic flow-through microbial fuel cells. Sci Rep 7(1):41208. https://doi.org/10.1038/srep41208
29. Kim IS, Chae KJ, Choi MJ, Verstraete W (2008) Microbial fuel cells: recent advances, bacterial communities and application beyond electricity generation. Environ Eng Res 13(2):51–65
30. Kuchi S, Sarkar O, Butti SK, Velvizhi G, Mohan SV (2018) Stacking of microbial fuel cells with continuous mode operation for higher bioelectrogenic activity. Biores Technol 257:210–216
31. Li W-W, Yu H-Q, He Z (2014) Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. Energy Environ Sci 7(3):911–924
32. Liang P, Duan R, Jiang Y, Zhang X, Qiu Y, Huang X (2018) One-year operation of 1000 L modularized microbial fuel cell for municipal wastewater treatment. Water Res 141:1–8
33. Light SH, Su L, Rivera-Lugo R, Cornejo JA, Louie A, Iavarone AT, Ajo-Franklin CM, Portnoy DA (2018) A flavin-based extracellular electron transfer mechanism in diverse gram-positive bacteria. Nature 562(7725):140–144. https://doi.org/10.1038/s41586-018-0498-z

34. Linke L (2018) Optimization of electrolytes and electrodes to improve performance of microbial fuel cells (MFC) and microbial desalination cells (MDC). National University of Singapore (Singapore)
35. Liu H, Logan BE (2004) Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. Environ Sci Technol 38(14):4040–4046
36. Liu H, Ramnarayanan R, Logan BE (2004) Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol 38(7):2281–2285
37. Logan B, Cheng S, Watson V, Estadt G (2007) Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. Environ Sci Technol 41(9):3341–3346. https://doi.org/10.1021/es062644y
38. Logan BE, Rossi R, Ragab A, Saikaly PE (2019) Electroactive microorganisms in bioelectrochemical systems. Nat Rev Microbiol 17(5):307–319. https://doi.org/10.1038/s41579-019-0173-x
39. Logan BE, Wallack MJ, Kim K-Y, He W, Feng Y, Saikaly PE (2015) Assessment of microbial fuel cell configurations and power densities. Environ Sci Technol Lett 2(8):206–214
40. Lovley DR (2008) The microbe electric: conversion of organic matter to electricity. Curr Opin Biotechnol 19(6):564–571. https://doi.org/10.1016/j.copbio.2008.10.005
41. Maktabifard M, Zaborowska E, Makinia J (2018) Achieving energy neutrality in wastewater treatment plants through energy savings and enhancing renewable energy production. Rev Environ Sci Bio/Technol 17(4):655–689. https://doi.org/10.1007/s11157-018-9478-x
42. Mardanpour MM, Esfahany MN, Behzad T, Sedaqatvand R (2012) Single chamber microbial fuel cell with spiral anode for dairy wastewater treatment. Biosens Bioelectron 38(1):264–269
43. Mateo S, Cantone A, Cañizares P, Fernández-Morales F, Scialdone O, Rodrigo M (2018) On the staking of miniaturized air-breathing microbial fuel cells. Appl Energy 232:1–8
44. Miran F, Mumtaz MW, Mukhtar H, Akram S (2021a) Iron oxide-modified carbon electrode and sulfate-reducing bacteria for simultaneous enhanced electricity generation and tannery wastewater treatment. Front Bioeng Biotechnol 9
45. Miran W, Naradasu D, Okamoto A (2021b) Pathogens electrogenicity as a tool for in-situ metabolic activity monitoring and drug assessment in biofilms. iScience 24(2):102068. https://doi.org/10.1016/j.isci.2021.102068
46. Mirhosseini A, Salvacion M, Chen S, Babanova S, Bretschger O (2016) Influence of anode configuration on flow distribution and performance in tubular microbial fuel cells. In: ECS Meeting Abstracts, vol 36. IOP Publishing, p 1841
47. Mohamed A, Ha P, Peyton B, Mueller R, Meagher M, Beyenal H (2019) In situ enrichment of microbial communities on polarized electrodes deployed in alkaline hot springs. J Power Sour 414:547–556. https://doi.org/10.1016/j.jpowsour.2019.01.027
48. Molderez T, Prévoteau A, Ceyssens F, Verhelst M, Rabaey K (2020) A chip-based 128-channel potentiostat for high-throughput studies of bioelectrochemical systems: optimal electrode potentials for anodic biofilms. Biosens Bioelectron 174:112813. https://doi.org/10.1016/j.bios.2020.112813
49. Muttitt G, Kartha S (2020) Equity, climate justice and fossil fuel extraction: principles for a managed phase out. Clim Policy 20(8):1024–1042. https://doi.org/10.1080/14693062.2020.1763900
50. Naradasu D, Guionet A, Miran W, Okamoto A (2020) Microbial current production from Streptococcus mutans correlates with biofilm metabolic activity. Biosens Bioelectron 162:112236. https://doi.org/10.1016/j.bios.2020.112236
51. Obileke K, Onyeaka H, Meyer EL, Nwokolo N (2021) Microbial fuel cells, a renewable energy technology for bio-electricity generation: a mini-review. Electrochem Commun 125:107003. https://doi.org/10.1016/j.elecom.2021.107003
52. Powell E, Evitts R, Hill G, Bolster J (2011) A microbial fuel cell with a photosynthetic microalgae cathodic half cell coupled to a yeast anodic half cell. Energy Sour Part A: Recov Utiliz Environ Effects 33(5):440–448

53. Qian F, Baum M, Gu Q, Morse DE (2009) A 1.5 μL microbial fuel cell for on-chip bioelectricity generation. Lab Chip 9(21):3076–3081. https://doi.org/10.1039/B910586G
54. Qian F, He Z, Thelen M, Li Y (2011) A microfluidic microbial fuel cell fabricated by soft lithography. Biores Technol 102:5836–5840. https://doi.org/10.1016/j.biortech.2011.02.095
55. Ren H, Lee HS, Chae J (2012) Miniaturizing microbial fuel cells for potential portable power sources: promises and challenges. Microfluid Nanofluid 13(3):353–381. https://doi.org/10.1007/s10404-012-0986-7
56. Ringeisen BR, Henderson E, Wu PK, Pietron J, Ray R, Little B, Biffinger JC, Jones-Meehan JM (2006) High power density from a miniature microbial fuel cell using Shewanella oneidensis DSP10. Environ Sci Technol 40(8):2629–2634. https://doi.org/10.1021/es052254w
57. Shin S-H, Choi Y-j, Na S-H, Jung S-h, Kim S-h (2006) Development of bipolar plate stack type microbial fuel cells. Bull Korean Chem Soc 27(2):281–285
58. Sivasankar V, Mylsamy P, Omine K (2018) Microbial fuel cell technology for bioelectricity. Springer
59. Srikanth S, Kumar M, Singh D, Singh M, Das B (2016) Electro-biocatalytic treatment of petroleum refinery wastewater using microbial fuel cell (MFC) in continuous mode operation. Biores Technol 221:70–77
60. Syzdlowski L, Ehlich J, Shibata N, Goryanin I (2021) High-throughput screening and selection of PCB-bioelectrocholeaching, electrogenic microbial communities using single chamber microbial fuel cells based on 96-well plate array. bioRxiv
61. Szydlowski L, Ehlich J, Goryanin I, Pasternak G (2022) High-throughput 96-well bioelectrochemical platform for screening of electroactive microbial consortia. Chem Eng J 427:131692
62. Tahernia M, Mohammadifar M, Gao Y, Panmanee W, Hassett D, Choi S (2020) A 96-well high-throughput, rapid-screening platform of extracellular electron transfer in microbial fuel cells. Biosens Bioelectron 162:112259. https://doi.org/10.1016/j.bios.2020.112259
63. Tahernia M, Mohammadifar M, Hassett D, Choi S (2019) A fully disposable 64-well papertronic sensing array for screening electroactive microorganisms. Nano Energy 65:104026. https://doi.org/10.1016/j.nanoen.2019.104026
64. Tan WH, Chong S, Fang H-W, Pan K-L, Mohamad M, Lim JW, Tiong TJ, Chan YJ, Huang C-M, Yang TC-K (2021) Microbial fuel cell technology—A critical review on scale-up issues. Processes 9(6):985
65. Tang RCO, Jang J-H, Lan T-H, Wu J-C, Yan W-M, Sangeetha T, Wang C-T, Ong HC, Ong ZC (2020) Review on design factors of microbial fuel cells using Buckingham's Pi Theorem. Renew Sustain Energy Rev 130:109878
66. Wang X, Feng Y, Lee H (2008) Electricity production from beer brewery wastewater using single chamber microbial fuel cell. Water Sci Technol 57(7):1117–1121
67. Watanabe K (2008) Recent developments in microbial fuel cell technologies for sustainable bioenergy. J Biosci Bioeng 106(6):528–536
68. Yang Y, Liu T, Tao K, Chang H (2018) Generating electricity on chips: microfluidic biofuel cells in perspective. Ind Eng Chem Res 57(8):2746–2758. https://doi.org/10.1021/acs.iecr.8b00037
69. Yang Y, Lu Z, Lin X, Xia C, Sun G, Lian Y, Xu M (2015) Enhancing the bioremediation by harvesting electricity from the heavily contaminated sediments. Biores Technol 179:615–618
70. Yano M, Tomita A, Sano M, Hibino T (2007) Recent advances in single-chamber solid oxide fuel cells: a review. Solid State Ionics 177(39–40):3351–3359
71. Zhang X, Cheng S, Huang X, Logan BE (2010) Improved performance of single-chamber microbial fuel cells through control of membrane deformation. Biosens Bioelectron 25(7):1825–1828
72. Zhang Y, Min B, Huang L, Angelidaki I (2011) Electricity generation and microbial community response to substrate changes in microbial fuel cell. Biores Technol 102(2):1166–1173
73. Zhou S, Wen J, Chen J, Lu Q (2015) Rapid measurement of microbial extracellular respiration ability using a high-throughput colorimetric assay. Environ Sci Technol Lett 2(2):26–30. https://doi.org/10.1021/ez500405t

Electrochemical Measurements of Microbial Fuel Cells (MFCs)

Mustapha Omenesa Idris, Asim Ali Yaqoob, Mohamad Nasir Mohamad Ibrahim, Nur Asshifa Md Noh, and Najwa Najihah Mohamad Daud

Abstract Electrochemical measurements are an important analytical survey performed to evaluate the overall power production performance of microbial fuel cells (MFCs). In recent years, MFCs research has experienced a strong interest in improving the energy performance by modifying the anode materials and increasing the activities of the electrogenic bacteria. Electrochemical measurements have become important evaluation tools for effective research of this development. Several of these metrics exist; however, their combination provides a more comprehensive view of MFC's performance. This chapter provides details on some of the electrochemical measurements used in MFCs and how to determine some of the electrochemical properties.

Keywords Microbial fuel cells · Electrochemical analysis · Cyclic voltammetry · Electrochemical impendence spectroscopy

M. O. Idris · A. A. Yaqoob (✉) · M. N. M. Ibrahim (✉) · N. N. M. Daud
School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia
e-mail: asimchem4@gmail.com

M. N. M. Ibrahim
e-mail: mnm@usm.my

M. O. Idris
e-mail: idris.mo@student.usm.my

M. O. Idris
Department of Pure and Industrial Chemistry, Kogi State University, Kogi State, P.M.B, 1008 Anyigba, Nigeria

N. A. M. Noh
School of Biological Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia
e-mail: nurasshifa@usm.my

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*, Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_4

1 Introduction

The term microbial fuel cells (MFCs) have been described as a bio-electrochemical system comprising mainly of microbes and electrodes that are capable of transforming chemical energy into energy in the form of electricity. The microorganism (electrochemical active bacteria) acts as a catalyst in the system that allows for simultaneous remediation of environmental pollutants and generation of electricity [1]. Bacteria are frequently used to catalyse the anodic half-reactions in different fuel cells and in particular, MFCs. Microbes in the anode chamber are responsible for oxidising the carbon source (reduced substrates), thereby, giving out electrons and protons in the process. The generated electrons are absorbed by the anode and then transmitted to the cathode via an external circuit, while the proton has migrated into the cathode chamber via the proton exchange membrane [2, 3]. One of the advantages of MFCs is their ability to use a wide range of biomass-derived anodes with long term durability, cost-efficient and large surface area to enhance the growth of microbes and surface attachment [4, 5]. Many different microorganisms have been used in MFCs, both as mixed and single strain cultures, such as *Geobacteracea, Desulfobulbus* or *Desulfovibrio* families, etc. [6, 7]. Nowadays, researchers have adopted several electrochemical measurement techniques to study the fundamental component and processes as well as the performance of the MFC [8]. The result obtained from the measurements will further provide an elaborate understanding of all the elements of the MFCs and allow for the identification of improvement in the power generation; to achieve this, it is vital to select the most appropriate electrochemical techniques for the MFC evaluation and assessment [9]. The most recent and widest applications of MFCs are primarily related to wastewater treatment, bioremediation, and power generation. The microbial aspect of the system is however a critical component in the process performance. These applications frequently employ complex bacterial communities that grow freely in the MFC anode from inoculums of various sources and produce higher power densities than pure cultures [10]. Similarly, modification of anode electrodes has shown effectiveness in enhancing the bioremediation and energy generation in MFC [11–13]. Yaqoob et al. [14] presented a critical analysis of new trends in anode modification for improving MFCs performance. All the above contributions by researchers can be adequately identified by subjecting the MFC systems to critical electrochemical measurements. Electrochemical measuring techniques are very necessary for analysing the limited performance of each component and for optimising the MFCs operation, thereby, enabling continuous improvements. In this chapter, contemporary electrochemical analytical tools of MFCs are being discussed. The evolutionary trends and background of the electrochemical measurements in MFCs have been highlighted. Furthermore, we attempted to discuss the areas in MFC's electrochemical properties that have not been adequately elaborated in previous papers.

2 Evolution of Electrochemical Measurements of MFCs

Potter [15] was the first scientist in 1911 to describe the potentiality of microbes to acquire electrical energy from their vital activities. In the research work, he used primitive versions of both analogue and digital process signals. An electromagnetic ammeter was used to measure the current output, evaluating the deflecting force induced by the electrical current (analogue), whereas the charge transported was counted (digital) using a morse condenser-mediated signal. Potter noted that a maximum voltage of 0.3–0.5 V was produced when glucose was used as substrate and platinum as an electrode with microorganism *Saccharomyces cerevisiae and Escherichia coli* as an inoculum source. The steady development of semiconductors over the twentieth century resulted in the discovery of various solid-state electronics (the transistor and integrated circuit are viable examples), which expanded the boundaries of electrical measurements, applications, and designs [16]. It was reported that Hans Wenking, in 1952, devised a three-electrode electrochemical system characterised by electrode potentials. The electrode potential was regulated using a feedback-controlled source of power, potentiostat and a reference electrode [17]. A potentiostat is an electroanalytical instrument that is designed to control the working electrode's potential in a multiple electrode electrochemical cell. It contains many internal circuits that allow it to function in this capacity. Sanchez et al. [18] carried out a review work on microbial electrochemical technology and reported that Andrew Kay first invented the digital voltmeter in 1954 which led to the improvement of accuracy and reduction in the cost of electrochemical measurements. Digital Voltmeter is an electrical equipment that can measure both the alternative current (AC) and direct current (DC) which is able to obtain values of potential difference that is flowing through the circuit. Following this trend, a series of researches were conducted until 1962 when Davis et al. [19] illustrated the demonstration of a concept for the generation of electricity employing various microorganisms in a system ascribed as MFCs. This development has led to a more robust research exploit on microbes as a promising source of electrical energy and has attracted interest in the academic, economic, and geo-political world. However, it was only lately that MFC-related systems and technologies gained widespread attention, owing to advancements in microbe identification and utilisation, electrode material innovations, system set up and configuration [20].

3 Electrochemical Background of MFCs

The major underlying principle of MFCs is the utilisation of microorganisms as a biocatalyst to simultaneously achieve bioremediation and bioelectricity generation, with absolute safety of the environment. At the anode chamber, the biocatalysts oxidise the organic substrate to produce carbon dioxide, protons, and electrons that are passed to the anodic surface. The cathode receives the transferred electrons

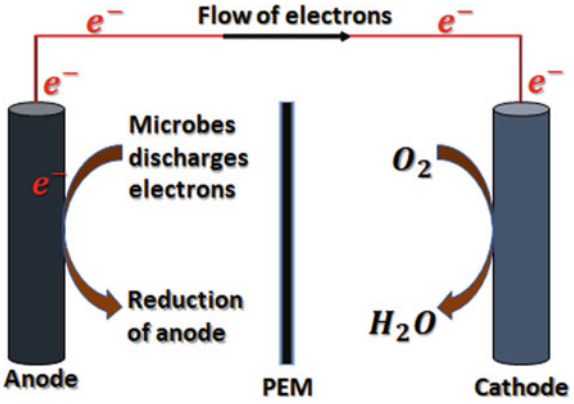

Fig. 1 Schematic show of electron flow from the anode to the cathode in MFCs

through an external circuit as shown in (Fig. 1), while the proton moves directly to the cathode through the proton exchange membrane. The electrochemical background in MFC entails the electroactivity between a working electrode and a microorganism which is usually faradaic, that is, the microorganism performs an external electron transfer (EET) process. The electron transport chains are elongated beyond the cell borders to facilitate electron discharge and uptake to a conductive electrode surface [21, 22].

The electrical equivalent circuit idea was employed to elucidate the MFC system's electrical output properties outside the cell boundary, microbial activities occurring in the cell, and general system bio-electrochemical behaviour [23]. As illustrated in (Fig. 2), a common equivalent circuit model for electrical characteristics of MFCs is composed of impedances in series: (a) illustrates the simplest equivalent circuit, which ignores dynamic characteristics, (b) illustrates a Randles circuit with the symbols R_{ct}, R_s, C_{dl}, and Z_w denoting the charge transfer resistance, ohmic resistance, double-layer capacitance, and Warburg diffusion element. This electrical impedance simulates the MFC's behaviour, particularly in terms of output voltage

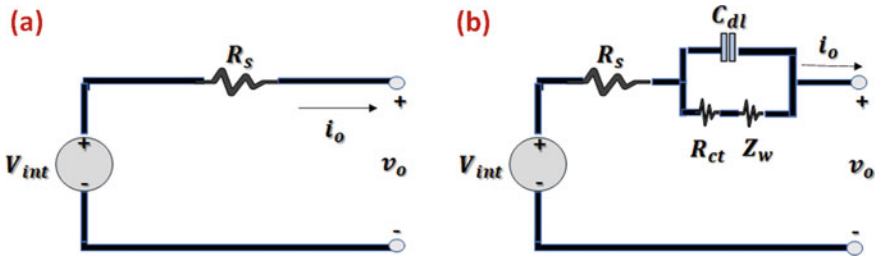

Fig. 2 Electric equivalent of a typical MFC circuit. **a** The simplest analogous circuit devoid of any dynamic property. **b** Equivalent Randles circuit having a Warburg diffusion element

and current. Electrochemical techniques such as electrochemical impendence spectroscopy (EIS), current interruption techniques, cyclic voltammetry, and polarisation testing are frequently employed nowadays to detect the equivalent circuit parameters and analyse electron transport [24].

Modern electrochemical systems can quickly shift signals from integrated analogue to digital converters to less sensitive digital counterparts (ADC). The differential amp amplifiers amplify differences between input voltage levels of the signal by means of a technique called common mode rejections that effectively reduces common interference such as ground loops. [25]. However, some differential amplifiers incorporate an initial unity gain amplifier as a voltage follower for every single input, thereby, reducing the load on the input signal and enabling the detection of low current signals [26].

4 Electrochemical Analysis

The electrochemical analysis is a series of analytical methods that analyse the chemical reactivity of an electrochemical system through electrical stimulation concepts. The rates of oxidation and reduction in electrochemical reactions are controlled and measured by a potentiostat, connected to electrodes that are submerged in an electrolyte. Collections of electrochemical techniques and their effect are shown in Table 1. Most of these techniques use three electrodes, designated as the working electrode (WE), the reference electrode (RE) and the counter electrode (CE). These three electrodes are connected to a potentiostat which in turn controls the WE potential to determine the output current [27]. The WE are the critical component in an electrochemical analysis. For instance, in most MFC processes, the anode is the WE while the cathode is applied as the counter electrode. Ag/AgCl is mostly used in the system as the RE.

4.1 Electrochemical Impendence Spectroscopy (EIS)

EIS technique is a simple measurement process that requires employing a Frequency Response Analyzer and a potentiostat. Typically, the range of frequency used in EIS is 100 kHz–1 MHz, and a very low-amplitude AC signal with an amplitude of about 5–10 mV is utilised to analyse the MFC's current response and not interfering with its operation. Such a low signal will not disturb the system due to a massive overpotential [28]. EIS is a robust instrument for analysing the chemical and physical processes occurring in electrochemical solutions, whether at solid–liquid or solid–solid interfaces, because it enables the separation of the various voltage loss occurrences. EIS makes use of two types of graphs: the graph Nyquist and the so-called Bode plots. The disadvantage of Nyquist plots is that the frequency represented by each data point is not disclosed (each point represents the vector of impedance on the complex

Table 1 Some MFC electrochemical chemical techniques and their effect

Electrochemical techniques	Remark	Advantages	Disadvantages
EIS	The quantity measured is Electrical impedance (Z) as a function of frequency. Occurs over a certain frequency range and AC signal amplitude	Capable of distinguishing between different sources of total internal resistance (Charge transfer, mass transport, electrolyte resistance)	Only applies to systems that are linear or quasi-linear. Basic fitting models make data analysis tough
Cyclic voltammetry	The quantity measured is $I = f(t)$ Occurs over a certain potential range and a scan rate (mV/s)	Most extensively used technique to study redox reaction that occurs on the surfaces of electrodes	In conventional cyclic voltammetry, the key issues are capacitance current and background charging current With rising voltage, fraction of the highest faradaic current and charging current drops
Current interruption (CI)	The cell is run at such a current that the polarisation concentration becomes negligible, giving way for a high signal to be achieved The immediate voltage rice after the current interruption is directly related to the internal ohmic resistance of the cell	Internal resistance of an electrochemical system is measured with this tool Magnetic and galvanic coupling measurement errors are easily identifiable The current interrupt is simple to use and can offer quantitative data	This value indicates only the overall ohmic drop over the electrode and is therefore only applicable in systems where ohmic resistance is the dominant resistance It is impossible to distinguish between mass transport, charge transfer and other ohmic losses
Polarisation curve	It depicts the relationship between current density (i) and electrode potential (E) for an MFC system	Details on the performance deterioration of each cell or stack under operating conditions are provided (Fuel flow rate, humidity, temperature, load)	Because the various contributions to the potential decrease overlap, analysing the underlying mechanism is difficult

plane at a certain frequency) while Bode plots do [29, 30]. MFCs EIS measurements are frequently done across a wide range of frequencies between a few MHz and 100 kHz. EIS spectra give detailed information on the mass transfer impedances, the charges and the ohmic internal resistance. The ohmic internal resistance is mostly studied by intersecting the curve at a high frequency with the actual impedance axis (Zre axis) [28]. Yaqoob et al. [31] applied electrochemical impedance spectroscopy to investigate the resistance effect of electrodes (EIS; Gamry Reference

600; Warminster, PA, USA). On Day 80 of the MFCs' operation, EIS measurements were taken to explore their electrochemical characteristics within the range of frequency (100 kHz–100 MHz). The continuous AC amplitude was 1 mV to prevent the biofilm from detaching. With a scene range of 0.5–0.1 Hz, each spectrum took about 15–20 min to complete.

Recent paper publications have demonstrated the utilisation of EIS in the evaluation of several electrochemical properties of the MFCs working electrodes under different operational conditions and the parameters that determine its power output. Dong et al. [32] studied a novel electrode prepared from activated carbon/PTFE composite for MFC performance. They applied an AC signal amplitude of 10 mV at a frequency range (10 MHz–100 kHz). Similarly, Hou et al. [33] evaluated the EIS of a modified Gr-Poly nanocomposite as a novel anode material having a surface area of 3.24 cm^2, with an applied AC wave amplitude of 10 mV and frequency range of 5 MHz–100 kHz. Fadzli et al. [34] used EIS as one of the electrochemical measurement tools to investigate the power performance of a benthic MFC. The EIS investigation was conducted using Gamry Reference 600, Warminster, PA, USA. In the EIS study, the frequency range was 100 kHz–100 MHz. Table 2 shows the list of some EIS experiments in MFCs.

Table 2 Some Electrochemical Impendence Spectroscopy analysis conducted in MFCs

Counter electrode (CE)	Working electrode (WE)	Reference electrode (RE)	Frequency range	AC Signal amplitude	Refs
Pt	Glassy carbon	Ag/AgCl	100 kHz–100 MHz	1 mV	Yaqoob et al. [11]
Graphite with Pt	Graphite	Ag/AgCl	100 kHz–5 MHz	10 mV	Manohar et al. [35]
Graphite felt	Platinum electrodeposited on carbon cloth	Ag/AgCl	100 kHz–5 MHz	10 mV	He et al. [36]
Carbon brush	Carbon brush	Standard calomel electrode	0.01 Hz–1 × 10^5 Hz	5 mV	Zhang et al. [37]
Activated carbon	Activated carbon	CP sheet	20 kHz–0.1 Hz	0.3 mA and six points per decade	Offei et al. [38]
Pt	Modified Carbon cloth	Ag/AgCl	0.1 Hz–1 × 10^5 Hz	0.2 V	Mishra and Jain [39]
Stainless steel	Polypyrrol stainless steel	Ag/AgCl	100 kHz–1 MHz	10 mV	Pu et al. [13]
Sterile carbon fibre	Carbon paper	Ag/AgCl	100 kHz–0.1 Hz	0.05 V	Arkatkar et al. [40]
Pt/C on CC	Iron modified carbon cloth	Ag/AgCl	100 kHz–100 MHz	0.2 V	Sayed et al. [41]

The capacitance between electrode and solution interface changes when the surface of the electrode is attached by a biofilm. This was confirmed by Manohar et al. [35] using EIS techniques. The EIS studies were performed at the OCP using a 100 kHz–5 MHz frequency range and a 10 mV ac signal amplitude. They discovered that in the present MR-1 species, the anode's OCP became more negative and its capacity increased; both affected the MFC power output.

4.2 Cyclic Voltammetry (CV)

Cyclic voltammetry has become one of the most popular tools for studying electrochemical reactions. CV is considered a flexible electroanalytical technique for the study of electroactive species. Its ease of measurement and flexibility has resulted in a wider range of use in the fields of electrochemistry. CV is a technique that entails cycling the voltage of an electrode in an electrochemical cell and determining the output current. The potential of this working electrode (WE) is regulated in relation to a reference electrode (RE) mostly a saturated calomel electrode (SCE) or an Ag/AgCl electrode. The controlling potential applied between these two electrodes can be thought of as an excitation signal [42].

CV has been widely used by researchers for MFCs application (Table 3). For example, Zhang et al. [43] tested for a novel anode material and used CV as one of the electrochemical analysing tools. The applied voltage range was 800–400 mV (around RE) with 10 mV/s as the scan rate. The WE were stainless steel mesh plated round with graphene; the CE was of carbon paper while the RE was Ag/AgCl. The authors were able to determine the electrocatalytic behaviour of the anode material through the CV analytical techniques. Similarly, Chen et al. [44] analysed the anode performance of MFC using electrochemical tests. Cyclic voltammetry (CV) was conducted with a voltage range of −0.8 to 0.8 V at a scan rate of 10 mV/s. Tafel plots of bioanodes were recorded by sweeping the overpotential from 0 to 0.1 V at 1 mV s^{-1}. The exchange current density (j_0, A/cm^2) was calculated via the Tafel equation. In another work, CV was also used to study the oxygen reduction catalytic behaviour of activated biochar in the MFC system. The voltage was in the range of −0.9 and 0.6 V with 5 mV/s as the scan rate. The electrical two-layer biochar capacity was evaluated with a CV curve recording in an N2-saturated environment and a charge current measuring in the absence of Faradaic contributions (at −0.1 V) based on the possible rate of sampling of 5–50 mVs^{-1}. A calomel electrode saturated (SCE, Amel 303/SCG/12) functioned as the electrode of reference, a platinum wire (Amel, 805/SPG/12) as an auxiliary electrode, and a glassy carbon disc (GC, 0.196 cm^2 area) as the working electrode (WE) modified with the catalyst layer [45]. Chorbadzhiyska et al. [46] investigated the performance of bioelectrodes using CV. They observed a difference in the cyclic voltammograms obtained with the different electrode types which show that electrode modifications influence the redox behaviour of the microbes and probably its biofilm formation strategies.

Table 3 Cyclic voltammetry analysis in different type of MFCs operations

Type of MFCs	Electrodes	Surface area of WE (cm^2)	Size of electrode (cm^3)	Voltage range (V)	Scan rate (mV/s)	Refs
Dual-chamber	WE: Graphite, CE: Graphite, RE: Ag/AgCl	–	8.0 × 2.5 × 0.2	−0.12 to +1.23	25 50	López Zavala et al. [47]
AC-MFCs	WE: Carbon clothe, CE: Carbon fibre bush, RE: Ag/AgCl	7.07	70 mm × 70 mm	−0.45 to +0.40	1	Ruiz et al. [48]
Dual-chamber	WE: Graphene/Ni, CE: Pt, RE: Ag/AgCl	2.0	2.0 × 1.3 × 0.1	−1.5 to + 0.7	20	Zhu et al. [49]
Single-chamber	WE: Carbon paste, CE: Platinum disc, RE: Ag/AgCl	0.5	–	−0.4 to + 1.2	50	Khater et al. [50]
Dual-chamber	WE: Carbon felt, CE: Pt/C paper, RE: Ag/AgCl	30	–	−0.65 to +0.25	1	Koók et al. [51]
Dual-chamber	WE: PANi/CNT, CE: SS mesh, RE: Ag/AgCl	–	3.0 × 2.0 × 0.1	−1 to +1	1	Yellappa et al. [52]
Dual-chamber	WE: GO, CE: SS mesh; RE: Ag/AgCl	20	–	−0.2 to + 0.8	50	Pareek et al. [53]
Single-chamber	WE: C-cloth, CE: Pt wire, RE: Ag/AgCl	20	–	−1 to +1	10	Khan et al. [54]
Single-chamber	WE: Carbon fibre brush, CE: C-Fibre brush, RE: Ag/AgCl	–	2.5 cm × 12 cm	−1 to +1	10	Yu et al. [55]
Double chamber	WE: Glassy carbon, CE: Pt wire, RE: Ag/AgCl	76 cm^2	8.0 cm × 1.3 cm	−0.8 to + 0.8	30	Yaqoob et al. [56]

4.3 Varying Circuit Resistance (VCR)

The varying circuit resistance (VCR) technique has been largely useful in MFC systems to acquire Polarisation Data that can further obtain the power curve. Polarisation data obtained by the VCR technique are applied to determine the effect of anode capacitance on the maximum power density of the system [57]. However, the VCR approach makes it challenging to achieve a steady-state anode potential. The cell potential is typically measured using the VCR method after the MFC has been operated continuously at a fixed resistance for 20 min; however, this time period may not be adequate to eliminate the influence of anode discharge if the anode has a high capacitance. As a result, the quantified power obtained using these techniques is referred to as transient power and not a steady-state power [58]. This point has been further illustrated in previous work [59]. Variations in external resistance in an MFC's external circuit can induce a variety of changes in performance, including changes in maximum current and power densities. Variation in external resistance has been demonstrated to impact the anode community in other investigations, most likely due to microbial adaptability [60]. Switching the R_{ext} will most likely change the anode potential, which has been proven to modify the expression of certain cytochromes by specific bacteria [61]. Furthermore, for batch-mode MFCs, decreasing R_{ext} may boost coulombic efficiency due to increased reactor current density and shorter cycles [62].

Feng et al. [59] proved that the discharge of high capacity bio-electrons in an anode significantly contributes to the recorded maximum density of power, even more so if the duration of the VCR approach at fixed resistance is insufficient for use. The VCR method was used to record the potential at various resistances (open circuit, 2000, 1000, 500, 250, 100, 50, and 25 Ω) for a period of 5–20 min. The potentiostat was operated in the two-electrode mode to acquire the polarisation curve, while the cathode serves as the working electrode; the anode functioned simultaneously as the reference and counter electrode. Huang et al. [63] determined polarisation and power density curves in a single chambered MFC system using the VCR method. In their analysis, the circuit was interrupted until the open circuit voltage (OCV) was stable, then a variable resistance box was connected to any external resistance between 10,000 and 200 Ω and stabilised for 20 min, and the output voltage (U) was recorded. According to Ohm's law, the power density reaches a maximum value at the point the external resistance of the choke is equivalent to the internal resistance of the choke, and the internal resistance of the choke can be determined. Zhao et al. [64] performed polarisation analysis on MFCs using the VCR technique. Prior to polarisation procedures, the MFCs were disconnected and left open circuit for a predetermined amount of time (defined as idle time, t_{oc}) using the VCR method. This method was used to determine the polarisation curves by varying R_{ext} from the highest point to the lowest and in the opposite manner. Polarisation curves were obtained at various t_d (0.25, 0.5, and 2 h) and t_{oc} values (0.17, 0.5, 1, 2 and 5 h). Additionally, polarisation tests were conducted utilising VCRs with a longer td of

8 h (designated as steady-state VCR, VCRs) to determine the steady-state MFCs' maximum power densities. According to (Eq. 1), the curves (for power density) were derived from the polarisation curves.

$$P = U \times I \tag{1}$$

4.4 Current Interruption Method (CI)

The Current Interruption (CI) technique is a widely used electroanalytical method for measuring the total ohmic resistance of electrochemical systems (e.g. MFCs). Current interruption is simple to perform and can provide quantitative information, which makes it exceptionally suitable for measurements on single cells and small fuel cell stacks [65]. It can be done with common, low-cost electronic equipment. It is evident that while the MFC appears to produce a constant output current at the terminal of the external resistor, the circuit is abruptly opened, resulting in a sudden increase in cell voltage (VR), followed by a gradual increase [58]. The resistive internal overpotential (R_{int}) of the MFC is responsible for the instantaneous rapid voltage rise. The following Eqs. (2) and (3) are useful for calculating the total internal resistance and ohmic resistance of the MFC cell respectively [8].

$$R_{\text{int}} = \frac{V_R}{I} \tag{2}$$

$$R_{\Omega} = \frac{\Delta U}{I} \tag{3}$$

where I, is the steady-state current before interrupt, ΔU represents a step rise in voltage after current interrupt.

By lowering the intrinsic resistance of carbon fibre brush anodes, Xie et al. [66] were able to increase the performance of MFCs. The ohmic resistance of the MFC system was determined by the current interruption method. The current interruption data were measured at a time interval of 0.1 s and indicated using a data acquisition system (NEWARE, Shenzhen, China). The ohmic resistance was calculated (using Eq. 3). Similarly, CI tests were used to study the ideal resistive component (R_{ohmic}) in the analysis of the electrochemical performance of an MFC system. The tests were performed at open circuit voltage (concentration polarisation is negligible) and a current pulse of 2 mA was applied for 2 s using the potentiostat [67]. The current interruption method was used in an MFC system that was operating in a steady-state, i.e. there was no current in the open circuit. Voltage changes (ΔU) increased abruptly; a continuous gradual increase was observed to follow immediately. A data acquisition system (DAQ2213, ADLINK, Beijing, China) with a sampling rate of 1000 Hz was utilised to record real-time data on ΔU between the electrodes. The

interruption of the current can be described as instantaneous because the interruption process lasted only 0.001 s. The ohmic resistance was also calculated (using Eq. 3), and 'I' signifies the current at a steady-state before the interruption [68].

4.5 Pulse-Width Modulation (PWM)

A pulse-width modulated system has a pulse input, a control input, and an output. The control input is used to change the pulse-width of the output signal. PWM's main objective is to maximise energy harvesting by adjusting the resistive load and taking advantage of the capacitive characteristics of the MFCs. In terms of energy generation, it has already been found that intermittent loading and unloading of MFCs can be beneficial as more energy can be generated than continuous loading [69]. Grondin et al. [70] previously demonstrated that by intermittently connecting and disconnecting the electrical load (external resistance), the power output of the MFC may be increased. This was further demonstrated by Coronado et al. [71] by increasing the MFC's power output through pulse-width modulated external resistance. The paper presents a strategy for intermittently connecting the electrical load by studying the MFC's frequency response between 0.1 and 1000 Hz and using the MFC at a sufficiently high frequency comparable to a pulse-width modulated connection of the external resistor. R_{ext} was connected to the MFC for the first half of each cycle and detached for the remainder of the cycle for each frequency examined, equating to a 50% duty cycle. The frequency tests were performed with R_{ext} values of 8 and 47 Ω.

5 Electrochemical Properties

The electrochemical properties of a material refer to its properties in an electrochemically corrosive environment, such as electrochemical potentials and reaction constants. These qualities dictate how materials react to corrosive oxidation and reduction processes, which increase the valence of metals (zero valence) to form ions (cations) or oxides (or other solid oxidation products). On the reduction side, processes may entail the reduction of water and oxygen to create hydroxide ions and/or reactive oxygen intermediates, in addition to a variety of other biologically derived compounds sensitive to redox reactions. The oxidation and reduction reactions (often referred to as the two half-cell reactions) are electrically connected via the metal and complete the circuit via the solution, resulting in currents (electronic and ionic) flowing through both phases [72, 73]. The electrochemical properties of a carbon material can be demonstrated by a potential window (measuring the voltage range between the cathodic and anodic current densities), monitoring reactivity with redox probes, evaluating durability, and estimating sensitivity from the calibration curve [74]. Electrochemical characterisation tools (discussed in the previous

section) have been developed to obtain information about electrochemical properties. These tools can be used to obtain electrochemical information about materials [75]. This section highlights some of these electrochemical properties applicable to MFC systems. Table 4 shows the electrochemical properties obtained in some MFCs studies.

5.1 Current Density

Current density, also known as electric current density, is defined as the amount of electric current that flows through a unit cross-sectional area and is related to electromagnetism. Ampere per square metre is the unit SI for electric current density. It is denoted by the letter '*J*'. The current density can be expressed by the formula:

$$J = \frac{I}{A} \tag{4}$$

where: J = Current density; I = Electric current flowing through a given material or conductor; A = Cross-sectional area of a material or conductor.

The output current of an MFC process can be deduced from the output voltage obtained from the digital multimeter instrument connected to the cell as described by Karuppiah et al. [76], while using anode surface area for calculating the current density (Eq. 4). Determining the current density in MFC helps researchers analyse the electrical performance of the cell across the anode [77].

5.2 Power Density

Power density is an important parameter in a power generating system like MFCs. Power density is mainly used as a crucial parameter to study the performance rate of MFCs [78]. The definition of power density in MFC applications is the power of generated energy per unit area of the working electrode (W/m^2) or per unit volume of the working electrode (W/m^3) [79]. Estrada-Arriaga et al. [80] in their MFC studies calculated output power P from the equation below

$$P = I \times V \tag{5}$$

where: P = Power (W); I = Electric current flowing through the electrode; V = Output Voltage of the MFC. Furthermore, the power density PD was calculated from (Eq. 6).

Table 4 Electrochemical properties of some MFCs studies

Reference	Tools	Conditions	Electrochemical properties	Values
Borole et al. [87]	Fluke multimeter model 83 delivers the voltage output at 50 Ω load	• Inoculum source: pre-enriched microbial consortium • Electrode size: 2.54 × 2.54 × 0.63 cm^3 • Surface area: 12.56 cm^2	Max. power density	580 W/m^3
			Max. current density	15.1 A/m^2
			Coulombic efficiency	90%
			Maximum energy conversion efficiency	54%
Gurav et al. [88]	Digital multimeter (Fluke Corporation, USA)	• Inoculum source:1% (*v/v*) seed culture *S. marisflavi* • Surface area: 2.25 cm^2	Maximum power density	52.80 mW/cm^2
			Max. current density	6.85 mA/cm^2
Larrosa et al. [89]	DVM891 Digital multimeter (HQ power, Germany)	• Inoculum source: Brewery wastewater diluted in domestic wastewater • Surface area: 4 cm^2	Maximum power density	1058mW/m^3
			Max. current density	551 mA/m^3
			Coulombic efficiency	25%
Zhang et al. [90]	Data acquisition system (2700, Keithley Instrument, OH)	• Inoculum source: clarifier overflow • Surface area: 7 cm^2	Maximum power density	52 ± 2 W/m^3
			Maximum current density	3.85 A/m2
			Coulombic efficiency	81%
Yaqoob et al. [91]	Digital multimeter (UNI-T, Model UT120, China)	• Inoculum: $Pb^{2+}$with pond WW • Size of electrode: 8.0 cm × 1.3 cm (h × r) • Surface area: 76 cm^2	Maximum power density	1.35 mW/m^2
			Current density	143 mA/m^2
Mutuma et al. [92]	Bio-Logic VMP300 potentiostat (Knoxville TN 37, 930, USA)	• Inoculum: Sludge (Biodigester plant) • Electrode: 1 × 1 cm • Surface area: 1.13 cm^2	Specific energy	10 Wh/kg
			Specific power	6.9 kW/kg
			Capacitance retention	84.5%
			Coulombic efficiency	99.84%
			Specific current	5 A/g

(continued)

Table 4 (continued)

Reference	Tools	Conditions	Electrochemical properties	Values
Geetanjali et al. [93]	Potentiostat (AUTOLAB-PGSTAT302N)	• Inoculum: Anaerobic cultures from sewage treatment plant • Electrode: 10 × 10 mm	Highest capacitance	47.27 F/cm^2
			Max. power density	1128mW/m^2
Yu et al. [94]	Multi-channel voltage recorder (RC1106C, Hangzhou Liance Group Ltd)	• Inoculum: Anaerobic sludge from wasterwater treatment Plant • Electrode size: 2.5 × 2.7 cm • Surface area:307.55 m^2/g	Max. voltage output	488 mV
			Max. power density	2381 mW/m^3
			Max. current density	8 × 10^{-6} A/m^2
			Specific capacitance	3670 F m^{-2}
Sawant et al. [95]	Digital multimeter (Agilent 34405A, Agilent Technologies, Inc., USA)	• Inoculum source: *Shewanellaoneidensis* • Electrode size:0.5 × 0.5 × 4.0 cm	Max. power density	35.74 W/m^3
			Charge storage capacity	799 F/g[1]
			Energy density	111 Wh/kg[1]
Iftimie et al. [96]	16-channel voltage collection instrument (Pico data logger ADC-24)	• Inoculum source: municipal wastewater • Size of electrode: 3 mm (diameter)	Max. power density	393.8 mW/m^2
			Max. voltage output	864.9 mV
Inoue et al. [97]	Gamry reference 600 Potentiostat	• Inoculum source: *G. sulfurreducens* • Electrode size: 10 × 10 mm	Max. power density	3.6 μW/cm^2
			Max. current density	6.8 μA
			Max. voltage output	390 mV
Ansari et al. [98]	Potentiostat (VersaSTAT 3, Princeton Research, USA)	• Inoculum source: Shewanellaoneidensis • Electrode size: 2.5 × 4.5 cm	Max. power density	0.0588 W/m^2
			Current density	2 A/g
			Max. capacitance	525 F/g
Gajda et al. [99]	ADC-24 (Pico Laboratories, UK)	• Inoculum source: Anaerobic sewage sludge • Surface area: 10 cm^2	Max. power density	54 W/m^3

(continued)

Table 4 (continued)

Reference	Tools	Conditions	Electrochemical properties	Values
Jain et al. [100]	Data logger (34972A, Keysight Technologies, USA)	• Inoculum source: Anaerobic sludge • Surface area: 16 cm^2	Highest power output	0.47 mW
			Coulombic efficiency	14.26%
Yaqoob et al. [101]	–	• Inoculum source: metal supplemented wastewater • Electrode size: 10 × 9.5 cm • Surface area: 76 cm^2	Max. current density	25.43 mA/m^2
			Max. power density	0.105 mW/m^2
			Specific capacitance @ 85th time interval (day)	

$$\mathrm{PD} = \frac{P}{A} \tag{6}$$

where: PD = Power density (W/m^2 or W/m^3); P = Power output (W); A = Surface area of the electrode (m^2 or m^3).

5.3 Coulombic Efficiency

The Coulomb efficiency (CE) of an energy storage system is the ratio between charge and discharge capacity under a fixed voltage window [81]. Coulombic efficiency (CE) is directly related to fuel cell efficiency. Therefore, a high CE means a longer cycle life of the fuel cell. CE refers to the efficiency with which charge electrons are transmitted. In an MFC system, as described by Yang et al. [82], CE is calculated at a given value of external resistance based on variation in concentration of chemical oxygen demand (COD) using the following equation.

$$\mathrm{CE} = \frac{\mathrm{Mo}_2 \int_0^{t_b} I\,dt}{\mathrm{Fb} V_{\mathrm{AN}} \Delta \mathrm{COD}} \times 100\% \tag{7}$$

where: CE = Coulombic efficiency; Mo_2 = Molar mass of oxygen; t_b = Operation time of 1 MFC cycle; b = Number of electron exchange per mole of oxygen; F = Faraday's constant; V_{AN} = Volume of anode chamber. The ΔCOD symbolise the difference between the COD of inflowing anolyte and outflowing anolyte. Chemical oxygen demand (COD) can be determined by the rapid digestion spectrophotometry method [83].

5.4 Capacitance Retention

The specific capacitance (C) in an MFC system, describes the integration over the entire data set per unit area of the working electrode. Specific capacitances can be derived from galvanostatic tests or from cyclic voltammetry curves. The constant charge–discharge tests are generally carried out to determine the specific capacitance [84]. Specific capacitances can be computed using galvanostatic experiments and deduced from (Eq. 8).

$$C = \frac{I\Delta t}{m\Delta V} \tag{8}$$

where: C = Specific capacitance $(F \cdot g^{-1})$; I = Discharge current (A); Δt = Discharge time (s); ΔV = Potential window (V); m = Mass of the working electrode (mg). Specific capacitances that are computed from cyclic voltammetry tests can be calculated from (Eq. 9).

$$C = \frac{1}{\mathrm{mv}(V_b - V_a)} \int_{V_a}^{V_b} I dV \tag{9}$$

where: C = Specific capacitance $(F \cdot g^{-1})$; v = Scan rate $(V \cdot s^{-1})$; V_b and V_a = High and low potential limit (V); I = Discharge current (A); m = Mass of the working (mg).

Lv et al. [85] studied the capacitance of a synthetic anode material using galvanostatic charge–discharge tests with a current load of 0.5 mA/cm^2 over a potential range of −0.6 to 0.3 V. Equation 10 derived the computation for the specific capacitance C(F/cm^2) from the CV curve.

$$C = \frac{I_{\text{charge-discharge}} \times t}{U_{\text{charge-discharge}} \times A} \tag{10}$$

where: $I_{\text{charge–discharge}}$ = charge–discharge current; t is the discharge time; $U_{\text{charge–discharge}}$ is the potential window, and A is the projected surface area of the anode. Similarly, Peng et al. [86] calculated the specific capacitance (F/cm^2) of the anode in their MFC studies as presented in (Eq. 11).

$$C = \frac{Q_a + Q_c}{2A\Delta E} \tag{11}$$

where Q_a (C) and Q_c (C) = sum of anodic and cathodic voltammetric charges; A = surface area of anode; ΔE (V) = range of potential drop during CV.

6 Future Prospect and Conclusion

Electrochemical measurements are crucial in examining the numerous processes that occur in MFCs. It is used to determine the quality of electron transportation rate and, as a result, the overall performance of MFCs in terms of energy generation via a single species of microbe or a coalition of microbes in the form of anodic and cathodic peaks. The MFC's bioelectricity production, the existence of redox mediators, and the emergence of electron transfer channels can all be monitored using electroanalytical methods. EIS, CV, LSV, and other electrochemical measurement techniques are based on the interaction of microorganisms and electrodes. These methods rely on microbes' electrochemical activity at electrode–electrolyte interfaces and support their detection of mediators and other redox phenomena, such as current peaks [102]. Recently, MFCs research has made significant progress in generating energy [103]; nevertheless, the electrochemical analytical tools used to analyse these advancements require greater attention [104]. The major goal of this chapter is to give the reader a better grasp of what electrochemical measurements they should use in their MFCs research. MFCs are complicated bio-electrochemical systems that cannot be fully comprehended by a single technique. As a result, it is necessary to combine electrochemical measures in order to have a deeper knowledge of the bio-electrochemical system's performance.

References

1. Yaqoob AA, Khatoon A, Setapar SHM, Umar K, Parveen T, Ibrahim MNM, Ahmad A, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10. https://doi.org/10.3390/catal10080819.
2. Schaetzle O, Barrière F, Baronian K (2008) Bacteria and yeasts as catalysts in microbial fuel cells: electron transfer from micro-organisms to electrodes for green electricity. Energy Environ Sci 1. https://doi.org/10.1039/b810642h
3. Logan BE, Rossi R, Ragab A, Saikaly PE (2019) Electroactive microorganisms in bioelectrochemical systems. Nat Rev Microbiol 17. https://doi.org/10.1038/s41579-019-0173-x
4. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S (2020) Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview. Biochem Eng J 164:107779. https://doi.org/10.1016/j.bej.2020.107779
5. Yaqoob AA, Ibrahim MNM, Umar K, Parveen T, Ahmad A, Lokhat D, Setapar SHM (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214. https://doi.org/10.5004/dwt.2021.26737
6. Zhang Y, Liu M, Zhou M, Yang H, Liang L, Gu T (2019) Microbial fuel cell hybrid systems for wastewater treatment and bioenergy production: synergistic effects, mechanisms and challenges. Renew Sustain Energy Rev 103. https://doi.org/10.1016/j.rser.2018.12.027
7. Moradian JM, Fang Z, Yong YC (2021) Recent advances on biomass-fueled microbial fuel cell. Bioresour Bioprocess 8. https://doi.org/10.1186/s40643-021-00365-7
8. Zhao F, Slade RCT, Varcoe JR (2009) Techniques for the study and development of microbial fuel cells: an electrochemical perspective. Chem Soc Rev 38. https://doi.org/10.1039/b819866g

9. Yaqoob AA, Ibrahim MN, Yaakop AS, Rafatullah M (2022) Utilization of biomass-derived electrodes: a journey toward the high performance of microbial fuel cells. App Water Sci 12(5). https://doi.org/10.1007/s13201-022-01632-4
10. Ishii S, Watanabe K, Yabuki S, Logan BE, Sekiguchi Y (2008) Comparison of electrode reduction activities of Geobacter sulfurreducens and an enriched consortium in an air-cathode microbial fuel cell. Appl Environ Microbiol 74. https://doi.org/10.1128/AEM.01639-08
11. Yaqoob AA, Ibrahim MNM, Yaakop AS, Umar K, Ahmad A (2021) Modified graphene oxide anode: a bioinspired waste material for bioremediation of Pb2+ with energy generation through microbial fuel cells. Chem Eng J 417:128052. https://doi.org/10.1016/j.cej.2020.128052
12. Peng L, You SJ, Wang JY (2010) Carbon nanotubes as electrode modifier promoting direct electron transfer from Shewanella oneidensis. Biosens Bioelectron 25. https://doi.org/10.1016/j.bios.2009.10.002
13. Yaqoob AA, Serrà A, Bhawani SA, Ibrahim MN, Khan A, Alorfi HS, Asiri AM, Hussein MA, Khan I, Umar K (2022) Utilizing biomass-based graphene oxide–polyaniline–Ag electrodes in microbial fuel cells to boost energy generation and heavy metal removal. Polym 14(4). https://doi.org/10.3390/polym14040845
14. Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C (2021) Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov 23. https://doi.org/10.1016/j.eti.2021.101579
15. Potter MC (1911) Electrical effects accompanying the decomposition of organic compounds. Proc R Soc London Ser B Contain Pap Biol Charact 84. https://doi.org/10.1098/rspb.1911.0073
16. Enke CG (2015) The analog revolution and its on-going role in modern analytical measurements. Anal Chem 87. https://doi.org/10.1021/acs.analchem.5b02405
17. Dölling R (1998) Hans Wenking, born August 18th, 1923 A problem-solver for electrochemists. Mater Corros 49. https://doi.org/10.1002/(sici)1521-4176(199808)49:8<535::aid-maco535>3.0.co;2-m
18. Sánchez C, Dessì P, Duffy M, Lens PNL (2020) Microbial electrochemical technologies: electronic circuitry and characterization tools. Biosens Bioelectron 150. https://doi.org/10.1016/j.bios.2019.111884
19. Davis JB, Yarbrough HF (1962) Preliminary experiments on a microbial fuel cell. Science (80) 137. https://doi.org/10.1126/science.137.3530.615
20. Yaqoob AA, Fadzli FS, Ibrahim MN, Yaakop AS (2022) Benthic microbial fuel cells: a sustainable approach for metal remediation and electricity generation from sapodilla waste. Inter J Environ Sci Technol 10. https://doi.org/10.1007/s13762-022-04236-2
21. Kracke F, Vassilev I, Krömer JO (2015) Microbial electron transport and energy conservation—The foundation for optimizing bioelectrochemical systems. Front Microbiol 6. https://doi.org/10.3389/fmicb.2015.00575
22. Lovley DR (2011) Powering microbes with electricity: direct electron transfer from electrodes to microbes. Environ Microbiol Rep 3. https://doi.org/10.1111/j.1758-2229.2010.00211.x
23. Kashyap D, Dwivedi PK, Pandey JK, Kim YH, Kim GM, Sharma A, Goel S (2014) Application of electrochemical impedance spectroscopy in bio-fuel cell characterization: a review. Int J Hydrog Energy 39. https://doi.org/10.1016/j.ijhydene.2014.10.003
24. Cooper KR, Smith M (2006) Electrical test methods for on-line fuel cell ohmic resistance measurement. J Power Sour 160. https://doi.org/10.1016/j.jpowsour.2006.02.086
25. Morrison R (2016) Grounding and shielding: circuits and interference. Ground Shield Circuits Interface
26. Ma WJ, Luo CH, Lin JL, Chou SH, Chen PH, Syu MJ, Kuo SH, Lai SC (2016) A portable low-power acquisition system with a urease bioelectrochemical sensor for potentiometric detection of urea concentrations. Sensors (Switzerland) 16. https://doi.org/10.3390/s16040474
27. Allen LRF, Bard J (2001) Electrochemical methods: fundamentals and applications, 2nd edn
28. Bard AJ, Faulkner LR (2019) Electrochemical methods fundamentals and applications Allen
29. Mei BA, Munteshari O, Lau J, Dunn B, Pilon L (2018) Physical interpretations of nyquist plots for EDLC electrodes and devices. J Phys Chem C 122. https://doi.org/10.1021/acs.jpcc.7b10582

30. He Z, Mansfeld F (2009) Exploring the use of electrochemical impedance spectroscopy (EIS) in microbial fuel cell studies. Energy Environ Sci 2. https://doi.org/10.1039/b814914c
31. Yaqoob AA, Serrà A, Ibrahim MNM, Yaakop AS (2021) Self-assembled oil palm biomass-derived modified graphene oxide anode: an efficient medium for energy transportation and bioremediating Cd (II) via microbial fuel cells. Arab J Chem 14. https://doi.org/10.1016/j.arabjc.2021.103121
32. Dong H, Yu H, Wang X, Zhou Q, Feng J (2012) A novel structure of scalable air-cathode without Nafion and Pt by rolling activated carbon and PTFE as catalyst layer in microbial fuel cells. Water Res 46. https://doi.org/10.1016/j.watres.2012.08.005
33. Hou J, Liu Z, Zhang P (2013) A new method for fabrication of graphene/polyaniline nanocomplex modified microbial fuel cell anodes. J Power Sour 224. https://doi.org/10.1016/j.jpowsour.2012.09.091
34. Fadzli FS, Rashid M, Yaqoob AA, Ibrahim MNM (2021) Electricity generation and heavy metal remediation by utilizing yam (Dioscorea alata) waste in benthic microbial fuel cells (BMFCs). Biochem Eng J 172. https://doi.org/10.1016/j.bej.2021.108067
35. Manohar AK, Bretschger O, Nealson KH, Mansfeld F (2008) The polarization behavior of the anode in a microbial fuel cell. Electrochim Acta 53. https://doi.org/10.1016/j.electacta.2007.12.002
36. He Z, Huang Y, Manohar AK, Mansfeld F (2008) Effect of electrolyte pH on the rate of the anodic and cathodic reactions in an air-cathode microbial fuel cell. Bioelectrochemistry 74. https://doi.org/10.1016/j.bioelechem.2008.07.007
37. Zhang J, Chu L, Wang Z, Guo W, Zhang X, Chen R, Dong S, Sun J (2020) Dynamic evolution of electrochemical and biological features in microbial fuel cells upon chronic exposure to increasing oxytetracycline dosage. Bioelectrochemistry 136. https://doi.org/10.1016/j.bioelechem.2020.107623
38. Offei F, Thygesen A, Mensah M, Tabbicca K, Fernando D, Petrushina I, Daniel G (2016) A viable electrode material for use in microbial fuel cells for tropical regions. Energies 9:1–14. https://doi.org/10.3390/en9010035
39. Mishra P, Jain R (2016) Electrochemical deposition of MWCNT-MnO2/PPy nano-composite application for microbial fuel cells. Int J Hydrog Energy 41:22394–22405. https://doi.org/10.1016/j.ijhydene.2016.09.020
40. Arkatkar A, Mungray AK, Sharma P (2021) Study of electrochemical activity zone of Pseudomonas aeruginosa in microbial fuel cell. Process Biochem 101. https://doi.org/10.1016/j.procbio.2020.11.020
41. Sayed ET, Alawadhi H, Elsaid K, Olabi AG, Almakrani MA, Bin Tamim ST, Alafranji GHM, Abdelkareem MA (2020) A carbon-cloth anode electroplated with iron nanostructure for microbial fuel cell operated with real wastewater. Sustainable 12. https://doi.org/10.3390/su12166538
42. Wang H-W, Bringans C, Hickey AJR, Windsor JA, Kilmartin PA, Phillips ARJ (2021) Cyclic voltammetry in biological samples: a systematic review of methods and techniques applicable to clinical settings. Signals 2. https://doi.org/10.3390/signals2010012
43. Zhang Y, Mo G, Li X, Zhang W, Zhang J, Ye J, Huang X, Yu C(2011) A graphene modified anode to improve the performance of microbial fuel cells. J Power Sour 196. https://doi.org/10.1016/j.jpowsour.2011.02.067
44. Chen W, Liu Z, Li Y, Xing X, Liao Q, Zhu X (2021) Improved electricity generation, coulombic efficiency and microbial community structure of microbial fuel cells using sodium citrate as an effective additive. J Power Sour 482. https://doi.org/10.1016/j.jpowsour.2020.228947
45. Pepè Sciarria T, de Oliveira MAC, Mecheri B, D'Epifanio A, Goldfarb JL, Adani F (2020) Metal-free activated biochar as an oxygen reduction reaction catalyst in single chamber microbial fuel cells. J Power Sour 462. https://doi.org/10.1016/j.jpowsour.2020.228183
46. Chorbadzhiyska E, Bardarov I, Hubenova Y, Mitov M (2020) Graphite-metal oxide composites as potential anodic catalysts for microbial fuel cells. Catalysts 10. https://doi.org/10.3390/catal10070796

47. López Zavala MÁ, Peña OIG, Ruelas HC, Mena CD, Guizani M (2019) Use of cyclic voltammetry to describe the electrochemical behavior of a dual-chamber microbial fuel cell. Energies 12. https://doi.org/10.3390/en12183532
48. Ruiz Y, Baeza JA, Montpart N, Moral-Vico J, Baeza M, Guisasola A (2020) Repeatability of low scan rate cyclic voltammetry in bioelectrochemical systems and effects on their performance. J Chem Technol Biotechnol 95. https://doi.org/10.1002/jctb.6347
49. Zhu W, Gao H, Zheng F, Huang T, Wu F, Wang H (2019) Electrodeposition of graphene by cyclic voltammetry on nickel electrodes for microbial fuel cells applications. Int J Energy Res 43. https://doi.org/10.1002/er.4351
50. Khater DZ, El-khatib KM, Hassan RYA (2018) Exploring the bioelectrochemical characteristics of activated sludge using cyclic voltammetry. Appl Biochem Biotechnol 184. https://doi.org/10.1007/s12010-017-2528-y
51. Koók L, Le Quéméner ED, Bakonyi P, Zitka J, Trably E, Tóth G, Pavlovec L, Pientka Z, Bernet N, Bélafi-Bakó K, Nemestóthy N (2019) Behavior of two-chamber microbial electrochemical systems started-up with different ion-exchange membrane separators, Bioresour Technol 278. https://doi.org/10.1016/j.biortech.2019.01.097
52. Yellappa M, Sravan JS, Sarkar O, Reddy YVR, Mohan SV (2019) Modified conductive polyaniline-carbon nanotube composite electrodes for bioelectricity generation and waste remediation. Bioresour Technol 284. https://doi.org/10.1016/j.biortech.2019.03.085
53. Pareek A, Sravan JS, Mohan SV (2019) Fabrication of three-dimensional graphene anode for augmenting performance in microbial fuel cells. Carbon Resour. Convers 2. https://doi.org/10.1016/j.crcon.2019.06.003
54. Khan N, Anwer AH, Ahmad A, Sabir S, Khan MZ (2020) Investigating microbial fuel cell aided bio-remediation of mixed phenolic contaminants under oxic and anoxic environments. Biochem Eng J 155. https://doi.org/10.1016/j.bej.2019.107485
55. Vu MT, Noori MT, Min B (2020) Conductive magnetite nanoparticles trigger syntrophic methane production in single chamber microbial electrochemical systems. Bioresour Technol 296. https://doi.org/10.1016/j.biortech.2019.122265
56. Yaqoob AA, Ibrahim MNM, Yaakop AS (2021) Application of oil palm lignocellulosic derived material as an efficient anode to boost the toxic metal remediation trend and energy generation through microbial fuel cells. J Clean Prod 314. https://doi.org/10.1016/j.jclepro.2021.128062
57. Zhu X, Tokash JC, Hong Y, Logan BE (2013) Controlling the occurrence of power overshoot by adapting microbial fuel cells to high anode potentials. Bioelectrochemistry 90. https://doi.org/10.1016/j.bioelechem.2012.10.004
58. Logan BE (2012) Essential data and techniques for conducting microbial fuel cell and other types of bioelectrochemical system experiments. ChemSusChem 5. https://doi.org/10.1002/cssc.201100604
59. Feng C, Lv Z, Yang X, Wei C (2014) Anode modification with capacitive materials for a microbial fuel cell: an increase in transient power or stationary power. Phys Chem Chem Phys 16. https://doi.org/10.1039/c4cp00923a
60. Jung S, Regan JM (2011) Influence of external resistance on electrogenesis, methanogenesis, and anode prokaryotic communities in microbial fuel cells. Appl Environ Microbiol 77. https://doi.org/10.1128/AEM.01392-10
61. Zhu X, Yates MD, Hatzell MC, Ananda Rao H, Saikaly PE, Logan BE (2014) Microbial community composition is unaffected by anode potential. Environ Sci Technol 48. https://doi.org/10.1021/es404690q
62. Rossi R, Hall DM, Wang X, Regan JM, Logan BE (2020) Quantifying the factors limiting performance and rates in microbial fuel cells using the electrode potential slope analysis combined with electrical impedance spectroscopy. Electrochim Acta 348. https://doi.org/10.1016/j.electacta.2020.136330
63. Huang G, Zhang Y, Tang J, Du Y (2020) Remediation of Cd Contaminated Soil in microbial fuel cells: effects of Cd concentration and electrode spacing. J Environ Eng 146. https://doi.org/10.1061/(asce)ee.1943-7870.0001732

64. Zhao W, Chen S (2018) Critical parameters selection in polarization behavior analysis of microbial fuel cells. Bioresour Technol Rep 3. https://doi.org/10.1016/j.biteb.2018.07.010
65. Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Microbial fuel cells: methodology and technology, Environ Sci Technol 40. https://doi.org/10.1021/es0605016
66. Xie Y, Ma Z, Song H, Wang H, Xu P (2017) Improving the performance of microbial fuel cells by reducing the inherent resistivity of carbon fiber brush anodes. J Power Sour 348. https://doi.org/10.1016/j.jpowsour.2017.02.083
67. Littfinski T, Nettmann E, Gehring T, Krimmler S, Heinrichmeier J, Murnleitner E, Lübken M, Pant D, Wichern M (2021) A comparative study of different electrochemical methods to determine cell internal parameters of microbial fuel cells. J. Power Sour 494. https://doi.org/10.1016/j.jpowsour.2021.229707
68. Liang P, Wang H, Xia X, Huang X, Mo Y, Cao X, Fan M (2011) Carbon nanotube powders as electrode modifier to enhance the activity of anodic biofilm in microbial fuel cells. Biosens Bioelectron 26. https://doi.org/10.1016/j.bios.2010.12.002
69. Fradler KR, Kim JR, Boghani HC, Dinsdale RM, Guwy AJ, Premier GC (2014) The effect of internal capacitance on power quality and energy efficiency in a tubular microbial fuel cell. Process Biochem 49. https://doi.org/10.1016/j.procbio.2014.02.021
70. Grondin F, Perrier M, Tartakovsky B (2012) Microbial fuel cell operation with intermittent connection of the electrical load. J Power Sour 208. https://doi.org/10.1016/j.jpowsour.2012.02.010
71. Coronado J, Perrier M, Tartakovsky B (2013) Pulse-width modulated external resistance increases the microbial fuel cell power output. Bioresour Technol 147. https://doi.org/10.1016/j.biortech.2013.08.005
72. Zhang G, Viney C (2020) Bulk properties of materials. Biomater Sci. https://doi.org/10.1016/b978-0-12-816137-1.00005-2
73. Brunski JB (2013) Metals: basic principles. Biomater Sci Introd Mater (3rd edn). https://doi.org/10.1016/B978-0-08-087780-8.00013-9
74. Uchiyama K, Yamamoto T, Einaga Y (2021) Fabrication and electrochemical properties of boron-doped SiC. Carbon (N. Y.) 174. https://doi.org/10.1016/j.carbon.2020.12.017
75. Choudhary YS, Jothi L, Nageswaran G (2017) Electrochemical characterization. Elsevier Inc., https://doi.org/10.1016/B978-0-323-46140-5.00002-9
76. Karuppiah T, Uthirakrishnan U, Sivakumar SV, Authilingam S, Arun J, Sivaramakrishnan R, Pugazhendhi A (2021) Processing of electroplating industry wastewater through dual chambered microbial fuel cells (MFC) for simultaneous treatment of wastewater and green fuel production. Int J Hydrog Energy. https://doi.org/10.1016/j.ijhydene.2021.06.034
77. Pan Y, Zhu T, He Z (2019) Energy advantage of anode electrode rotation over anolyte recirculation for operating a tubular microbial fuel cell. Electrochem Commun 106. https://doi.org/10.1016/j.elecom.2019.106529
78. Yaqoob AA, Parveen T, Umar K, Ibrahim MNM (2020) Role of nanomaterials in the treatment of wastewater: a review. Water (Switzerland) 12. https://doi.org/10.3390/w12020495
79. Pandit S, Das D (2017) Principles of microbial fuel cell for the power generation, in: Microb Fuel Cell Bioelectrochem Syst Convert Waste Watts. https://doi.org/10.1007/978-3-319-66793-5_2
80. Estrada-Arriaga EB, Hernández-Romano J, García-Sánchez L, Guillén Garcés RA, Bahena-Bahena EO, Guadarrama-Pérez O, Chavez GEM (2018) Domestic wastewater treatment and power generation in continuous flow air-cathode stacked microbial fuel cell: Effect of series and parallel configuration. J Environ Manag 214. https://doi.org/10.1016/j.jenvman.2018.03.007
81. Wang W, Wei X, Choi D, Lu X, Yang G, Sun C (2015) Electrochemical cells for medium-and large-scale energy storage: fundamentals, Adv Batter Med Large-Scale Energy Storage Types Appl. https://doi.org/10.1016/B978-1-78242-013-2.00001-7
82. Yang W, Zhang F, He W, Liu J, Hickner MA, Logan BE (2014) Poly(vinylidene fluoride-co-hexafluoropropylene) phase inversion coating as a diffusion layer to enhance the cathode

performance in microbial fuel cells. J Power Sour 269:379–384. https://doi.org/10.1016/j.jpowsour.2014.06.119
83. Cid CA, Stinchcombe A, Ieropoulos I, Hoffmann MR (2018) Urine microbial fuel cells in a semi-controlled environment for onsite urine pre-treatment and electricity production. J Power Sour 400. https://doi.org/10.1016/j.jpowsour.2018.08.051
84. Wang Y, Zheng H, Chen Y, Wen Q, Wu J (2019) Macroporous composite capacitive bioanode applied in microbial fuel cells. Chin Chem Lett. https://doi.org/10.1016/j.cclet.2019.05.052
85. Lv Z, Xie D, Li F, Hu Y, Wei C, Feng C (2014) Microbial fuel cell as a biocapacitor by using pseudo-capacitive anode materials. J Power Sour 246. https://doi.org/10.1016/j.jpowsour.2013.08.014.
86. Peng X, Yu H, Yu H, Wang X (2013) Lack of anodic capacitance causes power overshoot in microbial fuel cells. Bioresour Technol 138. https://doi.org/10.1016/j.biortech.2013.03.187
87. Borole AP, Hamilton CY, Vishnivetskaya TA (2011) Enhancement in current density and energy conversion efficiency of 3-dimensional MFC anodes using pre-enriched consortium and continuous supply of electron donors. Bioresour Technol 102. https://doi.org/10.1016/j.biortech.2011.01.045
88. Gurav R, Bhatia SK, Choi TR, Kim HJ, Song HS, Park SL, Lee SM, Lee HS, Kim SH, Yoon JJ, Yang YH (2020) Utilization of different lignocellulosic hydrolysates as carbon source for electricity generation using novel Shewanella marisflavi BBL25. J Clean Prod 277. https://doi.org/10.1016/j.jclepro.2020.124084
89. Larrosa-Guerrero A, Scott K, Head IM, Mateo F, Ginesta A, Godinez C (2010) Effect of temperature on the performance of microbial fuel cells. Fuel 89. https://doi.org/10.1016/j.fuel.2010.06.025
90. Zhang X, Cheng S, Wang X, Huang X, Logan BE (2009) Separator characteristics for increasing performance of microbial fuel cells. Environ Sci Technol 43. https://doi.org/10.1021/es901631p
91. Yaqoob AA, Ibrahim MNM, Umar K, Bhawani SA, Khan A, Asiri AM, Khan MR, Azam M, Alammari AM (2021) Cellulose derived graphene/polyaniline nanocomposite anode for energy generation and bioremediation of toxic metals via benthic microbial fuel cells. Polymers (Basel) 13. https://doi.org/10.3390/polym13010135
92. Mutuma BK, Sylla NF, Bubu A, Ndiaye NM, Santoro C, Brilloni A, Poli F, Manyala N, Soavi F (2021) Valorization of biodigestor plant waste in electrodes for supercapacitors and microbial fuel cells. Electrochim Acta. https://doi.org/10.1016/j.electacta.2021.138960
93. Geetanjali, Rani R, Kumar S (2019) Enhanced performance of a single chamber microbial fuel cell using NiWO4/reduced graphene oxide coated carbon cloth anode. Fuel Cells 19. https://doi.org/10.1002/fuce.201800120
94. Yu F, Wang C, Ma J (2018) Capacitance-enhanced 3D graphene anode for microbial fuel cell with long-time electricity generation stability. Electrochim Acta 259. https://doi.org/10.1016/j.electacta.2017.11.038
95. Sawant SY, Han TH, Ansari SA, Shim JH, Nguyen ATN, Shim JJ, Cho MH (2018) A metal-free and non-precious multifunctional 3D carbon foam for high-energy density supercapacitors and enhanced power generation in microbial fuel cells. J Ind Eng Chem 60. https://doi.org/10.1016/j.jiec.2017.11.030
96. Iftimie S, Dumitru A (2019) Enhancing the performance of microbial fuel cells (MFCs) with nitrophenyl modified carbon nanotubes-based anodes. Appl Surf Sci 492. https://doi.org/10.1016/j.apsusc.2019.06.241
97. Inoue S, Parra EA, Higa A, Jiang Y, Wang P, Buie CR, Coates JD, Lin L (2012) Structural optimization of contact electrodes in microbial fuel cells for current density enhancements. Sens Actuat Phys 177. https://doi.org/10.1016/j.sna.2011.09.023
98. Ansari SA, Parveen N, Han TH, Ansari MO, Cho MH (2016) Fibrous polyaniline@manganese oxide nanocomposites as supercapacitor electrode materials and cathode catalysts for improved power production in microbial fuel cells. Phys Chem Chem Phys 18. https://doi.org/10.1039/c6cp00159a

99. Gajda I, Greenman J, Santoro C, Serov A, Melhuish C, Atanassov P, Ieropoulos IA (2018) Improved power and long term performance of microbial fuel cell with Fe–N–C catalyst in air-breathing cathode. Energy 144. https://doi.org/10.1016/j.energy.2017.11.135
100. Jain S, Mungray AK (2021) Comparative study of different hydro-dynamic flow in microbial fuel cell stacks. Chin J Chem Eng 32. https://doi.org/10.1016/j.cjche.2020.10.016
101. Yaqoob AA, Ibrahim MNM, Umar K (2021) Biomass-derived composite anode electrode: synthesis, characterizations, and application in microbial fuel cells (MFCs). J Environ Chem Eng 9. https://doi.org/10.1016/j.jece.2021.106111
102. Yaqoob AA, Bakar MA, Kim HC, Ahmad A, Alshammari MB, Yaakop AS (2022) Oxidation of food waste as an organic substrate in a single chamber microbial fuel cell to remove the pollutant with energy generation. Sust Energy Technol Ass 1. https://doi.org/10.1016/j.seta.2022.102282
103. Yaqoob AA, Ibrahim MNM, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) Recent advances in anodes for microbial fuel cells: an overview. Materials (Basel). https://doi.org/10.3390/ma13092078
104. Idris MO, Kim HC, Yaqoob AA, Ibrahim MNM (2022) Exploring the effectiveness of microbial fuel cell for the degradation of organic pollutants coupled with bio-energy generation. Sust Energy Technol Ass 52. https://doi.org/10.1016/j.seta.2022.102183

Practical Limitations with Microbial Fuel Cell Technology

Nishat Tabassum, Nafisa Islam, and Shoeb Ahmed

Abstract Microbial fuel cells (MFC) provide dual benefits of energy and resource recovery, while being capable of handling a variety of contaminants. This is useful for industries that deal with effluents containing a mixture of different wastes and therefore need a robust waste management system. However, before the technology can be made viable at the field scale, limitations pertaining to cost, scale-up, and other operational factors, such as hydraulic retention time, fouling and process optimization, must be addressed. This chapter summarizes these various practical limitations and corresponding solutions that are convenient and cost-effective so that MFCs can be utilized alongside conventional technologies for effluent treatment. To put these ideas into perspective, operational conditions of recent pilot-scale studies have also been highlighted.

Keywords Electrode · Membrane · Stacking · Modularity · Optimization

N. Tabassum · N. Islam · S. Ahmed (✉)
Department of Chemical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh
e-mail: shoebahmed@che.buet.ac.bd

N. Tabassum
e-mail: ntabassum14@che.buet.ac.bd

N. Islam
e-mail: nafisaislam@che.buet.ac.bd

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_5

1 Introduction

Microbial fuel cells are a versatile technology that can recover resources (energy and by-products) from a variety of waste substances. Degradation of organic compounds, heavy metal remediation and recovery, and nutrient recovery have been successfully demonstrated in MFCs [61, 70]. With real wastewater from distinct types of industries, MFCs achieved up to 90–95% of COD removal and over 2 W/m^3 of power density [7, 52]. Persistent organic compounds such as polycyclic aromatic hydrocarbons and petroleum hydrocarbons have also been effectively destroyed using MFC technology [55, 76]. Despite the promise, there are several operational parameters that limit the technology's applicability as field-scale treatment units. The microbial processes are also impacted by the operational conditions [19], and since the mechanisms have not been fully elucidated yet, there is little understanding of how robustly MFC systems should be designed [36]. Most of the studies in this field have sought to improve power output, using novel electrode materials or catalysts [8, 42]. However, further research is needed to address costs and scale-up challenges, which are the major barriers in MFC implementation. Unless the technology is made more convenient and accessible, it is unlikely to be adopted. It is also imperative to run pilot-scale studies to understand which operational conditions are optimum for a given substrate [23]. The combination of the substrate and MFC system parameters has major impact not only on the treatment efficiencies but also on the power output, the impacts of these can be even more than the choice of microbial community [49]. In this chapter, these system parameters and operational barriers have been summarized, with emphasis on the advancements that can reduce the costs of operation. Recent pilot-scale studies have also been highlighted because these studies represent the state-of-the-art in large-scale MFC technologies and can shed light on what further improvements need to be made.

2 Operational Challenges Associated with MFCs

2.1 Cost-Effective Electrodes

Anodes need to support the biofilm while acting as the conduit for electron transfer, which makes them the most critical component of microbial fuel cells. Any change in their properties can have a dramatic impact on the performance of the fuel cell [62]. In fact, studies determined that the anode potential governed the specific biomass activity of the electrogenic microorganisms [2]. Optimization of electrode materials is therefore of interest, and a variety of techniques have been attempted—from experimenting with unconventional materials to modifying the surface of graphite electrodes with nano catalysts [4, 10, 15, 43, 93]. However, because most of these studies were conducted on a laboratory scale, it is difficult to assess how expensive these novel electrodes would be in practical settings [19]. The choice of anodes

for large-scale microbial fuel cells is limited, because in addition to being inexpensive, they must be durable. Stainless steel anodes are promising candidates and have demonstrated high power densities after modification with conductive polymers and activated carbon [69, 79]. Another low-cost alternative is biochar, which can be derived from a variety of wastes such as corn stover or waste wood [32, 77]. Although the power density for biochar anodes was only 6% lower than that with granular graphite anode, the cost of the anodes was 90% less [31]. While preparing the biochar through pyrolysis, smaller particle sizes should be targeted, since the size is inversely related to the power density [75]. Size also affects the specific surface area of the particles, which has a direct impact on adsorption efficiency and consequently, on the efficiency with which the biofilm adheres on the electrode [29]. A major limitation however is the negative surface charge of biochar that repels the negatively charged biofilm, and this requires surface modification to increase the cationic content on the biochar. Senthilkumar et al. used nickel ferrite nanorods to modify the surface charge of biochar anodes and discovered that the biofilm concentration was higher on these anodes because of the positive surface charge [67]. With biochar granules, the most feasible configuration for continuous treatment of waste streams would be the packed bed setup [37]. To ensure electrical conductivity within these beds, current collectors constructed from graphite, stainless steel, or copper must be embedded into the bed [37, 56]. Cation exchange membranes can also be eliminated in the packed bed configuration [41].

Among the redox processes occurring in an MFC, the oxygen-reduction-reaction (ORR) at the cathode is the rate-limiting step. Catalysts are therefore necessary, and current research is focused on finding alternatives to expensive noble metal catalysts. Activated carbon, with its high specific surface area, can be a viable alternative. MFCs operated for over a year using stainless steel cathodes that had been coated with activated carbon, achieved a maximum power density of >1700 mW/m^2. Although performance deteriorated over time, the cathodes could be regenerated by washing the cathodes and re-pressing the activated carbon layer at 17 MPa. This simple operation completely restored the activity of the cathodes [90]. Activated biochar derived from sewage sludge also led to power densities on par with platinum cathodes [88]. In fact, addition of coconut shell to the biochar raised the power output to almost 2.4 times that of the platinum cathode [87]. Copper has also shown promise as a low-cost catalyst [8]. In a field-scale MFC having a 25 L anode chamber, carbon felt cathodes with a coating of Cu–Zn microparticles achieved an average power density that was 8 times that of the control. Long-term operation was feasible, while energy recovery per unit cost was almost 8-fold higher than MFCs containing platinum-coated cathodes [13]. Biotic cathode can be an alternative strategy, where a biofilm mediates the reduction of contaminants such as heavy metals and nitrates [39, 92], and power densities as high as 430 W/m^3 have been reported [36]. Convenient techniques have been adopted to create biocathodes, and electrodes can simply be inoculated as the anode before transferring them to the cathode chamber [63, 81].

2.2 Low-Cost Membranes and Membraneless Systems

Membranes constitute 60% of the total capital cost of MFCs [22], and the slow transfer of cations across the proton exchange membranes can create a charge imbalance, which leads to voltage losses [3, 66, 96]. This problem is more pronounced in wastewaters that tend to have elevated levels of K^+, Ca^{2+}, and Mg^{2+}. Membrane fouling (both by the biofilm and salt precipitates) also deteriorates the membrane's integrity over time [82]. Membraneless designs are less complex, cost less, and have been successfully implemented in field-scale units for mostly remediation purposes. A 350 L membraneless MFC was used to remove refractory polycyclic aromatic hydrocarbons from polluted water and the sediment bed, which achieved 89% and 70% reduction in total organic carbon content from the two phases [44]. However, power output gradually declined. This is a common concern with membraneless systems where salt precipitates can eventually form on the cathode [28, 37], in fact, salt precipitation was responsible for ~53% reduction in the power output [6]. Furthermore, without membranes, oxygen can infiltrate the anode chamber and induce aerobic oxidation of the organic compounds, thus suppressing electrogenic electron transfer [71]. Internal ionic short-circuiting due to anolyte-catholyte mixing is another performance-limiting phenomenon [95]. Membraneless designs are attractive only when replacing the membrane is challenging, for example, when the MFC is designed to remove pollutants from sediments or soil [44, 54]. If the configuration is to be adopted as a continuous treatment unit, the MFC has to be constructed so that either the electrodes are in separate chambers but have a channel that allows proton exchange, or laminar flow is maintained that prevents mixing of the electrolytes [5, 18]. Such architecture is not suitable for practical settings [5]. Furthermore, the bioanode performance ultimately drops as the oxygen infiltration causes methanogenic bacteria to dominate the anode chamber [59]. This would remove the additional advantage that MFCs have over traditional treatment units, which is the benefit of energy recovery from the wastes. Because of these limitations, a better strategy would be developing inexpensive membranes instead of optimizing membraneless configurations. To that end, a variety of materials have been explored, among which ceramic has been more extensively studied [86]. Ceramic membranes operate on the basis of size exclusion, which eliminates the concern of pH imbalance associated with selective cation transport, while reducing the overall internal resistance of the cell [11, 46]. Other low-cost materials have found success as well. A 90 L MFC was operated using cloth separators and operated using real brewery wastewater. The electrical output was sufficient to power the pumping system, releasing up to 0.034 kWh/m^3 of influent [17]. Between plastic grid, J-cloth (household cleaning cloth), and baking paper, the grid separator maintained the pH balance and achieved the highest power density (6 W/m^2). However, it allowed oxygen infiltration into the anode chamber, which led to a gradual decrease in power output as the bioanode performance deteriorated. In addition, biofouling was observed on the cathodes [59]. In a proof-of-concept study, eggshell membranes displayed a maximum power

density of 1440 mW/m^2 [51]. Compared to Nafion membranes, eggshell membranes had an internal resistance that was 8.6 times less, while costing a negligible amount since eggshells are waste materials [12]. Biochar membranes also generated 26 times higher power output than Nafion per unit cost of the membrane [9]. Although there are low-cost options, their feasibility in industrial wastewater treatment has not been proven yet. To combat the problem of membrane fouling, certain measures that limit the amount of hardness ions or excessive growth of biofilm should be adopted [35].

3 Scale-Up and System Configuration

Direct volumetric scale-up diminishes the energy output of an MFC since internal resistance increases in proportion [34, 89]. Feng et al. developed four 250 L modules for the treatment of municipal wastewater, which achieved limited power densities (0.47 W/m^3) due to the high internal resistance and a COD removal rate of 70–79% [18]. However, a 1000 L system consisting of 50 modules removed 70–90% of the COD and the power density was 7–60 W/m^3 [48]. Thus, scale-up using several miniature MFC units is a more effective method (Fig. 1), as it maintains the diffusion distances near the electrodes while increasing the total electrode surface area [24]. The electrical connection can be either series or parallel, with the series connection having the lowest operating cost to maximum power ratio, which is half that of parallel configurations [53]. However, if the cells are all immersed in a common electrolyte, it can also lead to ionic short-circuiting [60]. Therefore, the modules must not have any hydraulic connection between them [95]. A few studies have determined ways to solve this problem without physically separating the chambers. Zhuang et al. developed a low-cost 10 L serpentine-type MFC stack, where two rows of MFC units were arranged in parallel but had a series electrical connection. A maximum power density of 4.1 W/m^3 was obtained within the operating period of 180 days. 87.1% of the COD and 86% of the ammonium-nitrogen was removed from the brewery wastewater substrate [94]. In fact, stacking the modules in parallel arrangement not only reduces the system's physical footprint, but it can also induce chemical stratification that keeps the anolyte and catholyte chemically different, while the vertical orientation prevents any back-mixing. This self-stratification allows the system to be operated without a membrane [74]. Another approach used internal baffles to direct the flow from one cell to another without any back-mixing; this technique would however require recycling the substrate fluid after each passage. Although power output was found to be sufficient, this method has potential in treatment operations [60].

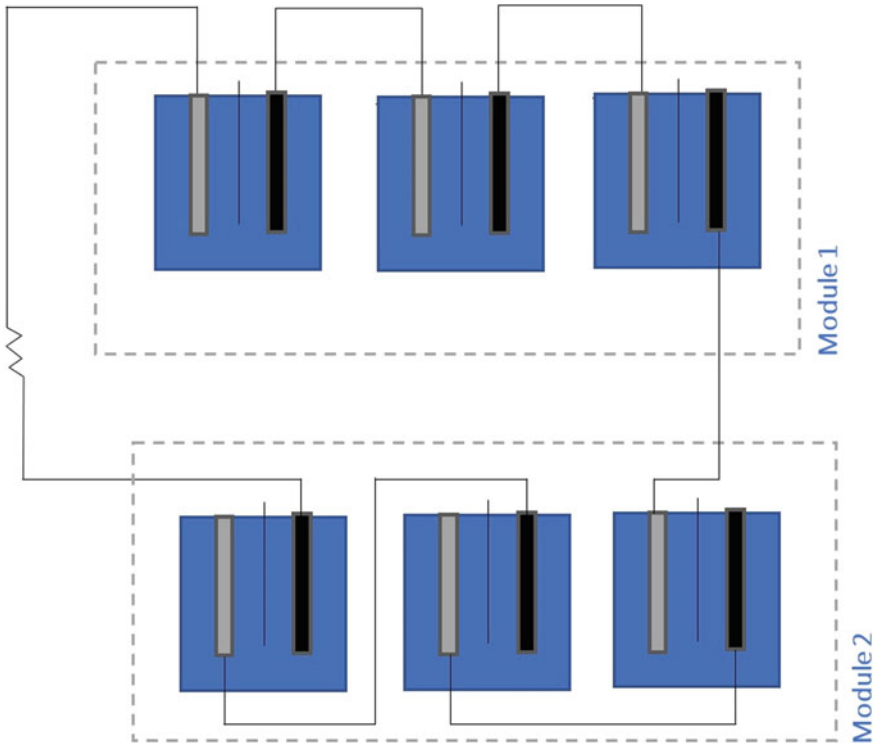

Fig. 1 Stacked modules in series electrical connection

4 Maintenance and Optimization Issues

Fouling of cathodes due to salt precipitates, humic acids, and biofilm can degrade performance of the MFCs over time [65, 84], which is especially challenging to remedy if there are several modules stacked together with minimal distance between them [64]. Fouling leads to blocking of the active sites of the catalyst layer on the biofilm, reducing the active surface area by as much as 12% [84]. Rossi et al. found that the performance of the cathode dropped by 63% in large-scale MFCs that had been operated for a month. After simply scraping off the biofilm that had accumulated on the cathode, 89% of the cathode potential was restored [64]. However, simply scraping off the biofilm is a laborious process. Rossi et al. utilized magnets to physically dislodge the biofilm from the cathode, but its applicability in large-scale systems has to be assessed [65]. Cathodes can also be modified to limit fouling. Yang et al. used polyvinylidene (PVDF) to bond cloth separators to cathodes, discovering that the maximum power density had reached 190 mW/m^2, which was 220% higher than cathodes without the separators bonded to them [83]. Salt precipitates usually

form when the catholyte evaporates leaving the precipitates behind on the cathode surface. Pulse-feed regimes can not only replenish the system with fresh substrate and maintain the power output [74], but it can also keep the cathodes hydrated, preventing precipitate layers from developing [72]. The extent of salt fouling also depends on the composition of the wastewater, decrease in power density would not be high if the salt concentrations are low [28]. Air-cathodes can also be enclosed within a chamber that allows sufficient air transfer without drying out the cathode. This modification ensures that the alkaline solution that is generated in the cathode does not evaporate leaving salt precipitates behind. The catholyte can be collected and as the liquid trickles down the cathode, it carries with it any salt deposits [19]. It is also possible to control salt precipitation if the waste stream is pretreated to reduce the levels of hardness ions, which is feasible if the MFC is integrated with other treatment units.

To avoid voltage losses due to a pH imbalance, buffers can be used to so that the pH does not change dramatically. Addition of buffer salts may not be necessary however, if the substrates already have a high concentration of ammonium ions [91]. Higher buffer capacity can also prevent the onset of salt fouling [96]. Other considerations depend on the type of impurities in the substrate. High levels of heavy metals can be toxic to the biofilm [1, 38]. Heavy metals can also inhibit the reduction of nitrates at the cathodes [78]. Cation exchange membranes allow superior recovery of nutrients (over 95%), both for ammonium-nitrogen and phosphates [85]. The hydraulic retention time (HRT) needs to be properly adjusted as well. For instance, although increasing the HRT improved treatment efficiencies [14, 73], it resulted in substrate depletion, which at low levels can lead to voltage reversal. Lu et al. determined a dramatic decrease in power output when the HRT was raised [50]. The dynamic changes in the load entering effluent treatment plants can lead to a fluctuating power output from MFCs. To manage this, use of capacitors that can store the electricity and discharge it when necessary have been proposed. These power management circuits can supply power from MFC systems in a controlled and stable manner and have been shown to increase voltages by over 70% [21]. A field-scale stacked MFC produced a maximum power of 61 mW and consisted of 12 supercapacitors (500 F) in the external circuit, which were sufficient to power 6 LED bulbs for 60–90 min every night [14]. An innovative setup by Nguyen et al. employed multiple MFCs, where each was connected to its own capacitor and a switch that maintained the operating point of the MFC at its maximum power point. A step-up converter boosted the voltage levels, leading power conversion efficiencies over 80% [58].

5 Process Integration and Large-Scale Studies

The most feasible way to use MFCs for waste treatment would be to integrate them with other treatment units. Li et al. envisioned a wastewater refinery that primarily relies on MFCs (Fig. 2). Pre-treatment would involve reducing solid waste and salts

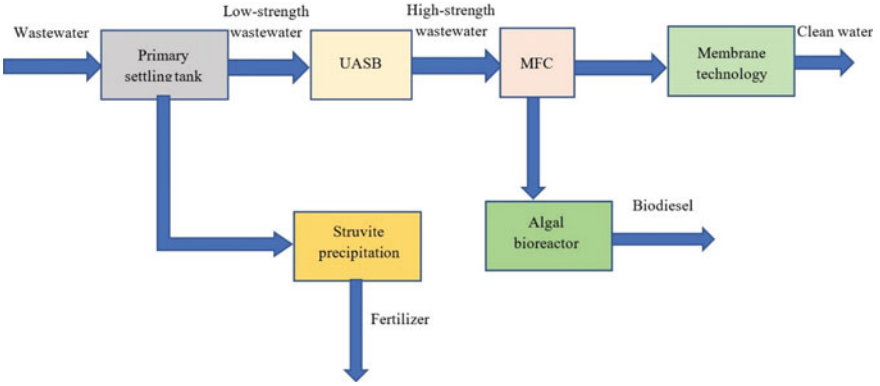

Fig. 2 Process block diagram of an MFC-centered wastewater refinery. Reproduced from reference with permission from the Royal Society of Chemistry [47]

using sedimentation. If the effluent has a low organic load, it can then be treated in an MFC directly; higher strength wastewaters may first need to be treated in an anaerobic bioreactor [47]. When a single-chamber MFC was combined with a low-cost flocculation unit, 97% of the COS and 99.1% of the ammonia-nitrogen was removed from swine wastewater, at an overall cost benefit of \$0.026 per m^3 of wastewater [16]. Phosphate-rich streams should be directed to a separate MFC that is designed for maximizing phosphate recovery by forming struvite ($MgNH_4PO_4 \cdot 6H_2O$), which is a potent, slow-release fertilizer [33]. Struvite forms at the high pH zone surrounding the cathodes and precipitation is enhanced if cation exchange membranes are used [85]. Algal treatment of the MFC effluent can improve the effluent quality and further reduce the nutrient levels [26]. Additional benefit includes biofuel production [40]. It is also possible to combine MFCs and algal reactors into a synergistic system, and Gajda et al. inoculated the cathode chamber of an MFC using algae and operated the unit as an MFC. The algae produced enough oxygen in situ for the reduction reaction, while generating more biomass that was directed into photoreactors. The mature biomass was then redirected into the anode, where it was broken down by the electrogenic bacteria. Such an arrangement can support power generation for over 25 days [20]. To produce clean water that meets discharge standards, the MFC outlet can be directed into a membrane filtration process or a membrane bioreactor. Pretreatment in an MFC reduced sludge production (<350 mg/L TSS), and the effluent COD was below 20 mg/L [30]. An overview of the various MFC-membrane bioreactor configurations have been discussed elsewhere [45].

The wastewater refinery concept, though promising, suffers from the drawbacks that still hold back MFC technology in the large-scale. Each unit requires a different quality of influent based on its operation target (e.g., a high organic load for either increased power output, biomass production, or nutrient recovery). Additional maintenance issues will arise; membranes are prone to fouling; self-shading may limit algae growth; and toxic metals may be incorporated within the struvite precipitate

[47]. These challenges necessitate robust process monitoring and control systems. A better understanding of the mechanism of action of the electrogenic microorganisms would lead to improved electrode design and optimization of process parameters that sustain the growth of these organisms [68]. Before process integration, use of MFCs in a large scale with real wastewaters must be assessed. One of the first pilot-scale studies using a large-scale MFC was conducted at Foster's brewery in Queensland. A 1000 L MFC consisting of 12 tubular modules achieved a power density of 8.5 W/m^3, however the cathodes degraded quickly due to biofilm and salt fouling [48]. Since then, progress in pilot-scale studies has been steady and many of these limitations have been addressed. He et al. developed a 6.1 L MFC system consisting of four anode modules and three (two-sided) cathode modules and tested it at different configurations. On alternating the modules through which the influent entered every other day, a maximum power density of 6.0 W/m^3 was achieved when the anodes were connected to two cathodes. COD removal was over 52% for both series and parallel flow configuration [25]. Several other pilot-scale studies operated with real waste where the reactor volume was more than 10 L have been summarized in Table 1.

The success of these pilot-scale units indicates that the technology is steadily making progress. Instead of the microbial chemistry, greater emphasis should be placed on the architectural and operational issues summarized in this chapter so that the technology can be used with other treatment units [57].

6 Conclusion and Future Perspectives

The barriers that prevent the adoption of MFCs should not be a reason to overlook this versatile and convenient technology, where waste can not only be treated, but it can be valorized. Stacking several modules is the key to scalability. However, to reduce the footprint, focus should be on making compact-sized units, consisting of low-cost materials as electrodes and membranes. Clearly, materials design is a critical research area within the field. Other considerations include extracting the generated power more efficiently using energy storage systems and developing robust process monitoring tools because of how dynamic MFCs are. Before implementing MFCs as effluent treatment units, studies must first assess the operational parameters that are most suitable for treatment. This knowledge can help in designing MFC systems that have longevity. Solving these technical challenges, in addition to developing technologies that integrate well with MFCs, should be prioritized. Extensive pilot-scale studies are also necessary to fully understand the performance issues.

Table 1 Recent advancements in pilot-scale MFCs

Type of unit	Reactor volume (L)	Power density	Electrode materials	Pollutant removal rates	Operation time	References
2 multi-panel systems with 16 single cathodes each	255	0.317 W/m^3	Anode: Graphite fiber brush Cathode: Stainless steel and activated carbon	COD: 41 ± 16% TSS: 36 ± 16% TN: 18 ± 14%	98 days	Hiegemann et al. [28]
2 tubular modules in series flow configuration	20	0.44 W/m^3	Carbon cloth (cathodes used without any catalyst)	COD: 94.6 ± 1%	>12 months	Lu et al. [50]
50 stacked modules	1000	7–60 W/m^3	Granular Activated Carbon with titanium screws as current collectors	COD: 70–90%	1 year	Liang et al. [48]
96 tubular modules in series electrical connection	200	0.72* A/m^3 (maximum)	Anode: Carbon brush Cathode: Carbon cloth (nitrogen doped activated carbon catalyst)	Total COD: 76.8% TSS: 91.4% Ammonium nitrogen: 68%	>300 days	Ge and He [22]
5 stacked modules in a baffled chamber	90	171 ± 8.4 mW/m^2 [a]	Anode: Carbon crush Cathode: Activated carbon	COD: 84–88% TSS: 81–86%	>6 months	Dong et al. [17]
3 flat-panel modules	72	25.6–42.1 W/m^3	Granular activated carbon with titanium mesh as current collectors	COD: 78–97%	~6 months	Wu et al. [80]

(continued)

Table 1 (continued)

Type of unit	Reactor volume (L)	Power density	Electrode materials	Pollutant removal rates	Operation time	References
4 membraneless modules	45	20 mW/m^2 (with respect to cathode area)	Anode: Graphite fiber brush Cathode: Carbon cloth-Graphite	COD: 24% TSS: 40% TN: 28%	9 months	Hiegemann et al. [27]
6 stacked modules under parallel electrical connection	115	1.9 ± 0.6 W/m^3	Stainless steel	COD: 40 ± 15% BOD: 95% Nitrates: 56 ± 15%	>6 months	Vilajeliu-Pons et al. [73]
6 stacked modules	720	3.79–7.29 mW/m^2	Anode: Carbon felt with goethite as catalyst Cathode: Carbon felt coated with transition metal complexes	COD: 87 ± 7%	255 days	Das et al. [14]

[a] Not mentioned whether with respect to anode or cathode area; * Current density
COD: chemical oxygen demand; TSS: total suspended solids; TN: total nitrogen

References

1. Abourached C, Catal T, Liu H (2014) Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Res 51:228–233. https://doi.org/10.1016/j.watres.2013.10.062
2. Aelterman P, Freguia S, Keller J et al (2008) The anode potential regulates the bacterial activity in microbial fuel cells. Commun Agric Appl Biol Sci 73:85–89
3. Akieh MN, Ralph SF, Bobacka J, Ivaska A (2010) Transport of metal ions across an electrically switchable cation exchange membrane based on polypyrrole doped with a sulfonated calix[6]arene. J Membr Sci 354:162–170. https://doi.org/10.1016/j.memsci.2010.02.052
4. Alatraktchi FA, Zhang Y, Noori JS, Angelidaki I (2012) Surface area expansion of electrodes with grass-like nanostructures and gold nanoparticles to enhance electricity generation in microbial fuel cells. Bioresour Technol 123:177–183. https://doi.org/10.1016/j.biortech.2012.07.048
5. Amirdehi MA, Khodaparastasgarabad N, Landari H et al (2020) A high-performance membraneless microfluidic microbial fuel cell for stable, long-term benchtop operation under strong flow. ChemElectroChem 7:2227–2235. https://doi.org/10.1002/celc.202000040
6. An J, Li N, Wan L et al (2017) Electric field induced salt precipitation into activated carbon air-cathode causes power decay in microbial fuel cells. Water Res 123:369–377. https://doi.org/10.1016/j.watres.2017.06.087
7. Behera M, Jana PS, More TT, Ghangrekar MM (2010) Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH. Bioelectrochemistry 79:228–233. https://doi.org/10.1016/j.bioelechem.2010.06.002
8. Bhattacharjee U, Pandey LM (2020) Novel nanoengineered materials-based catalysts for various bioelectrochemical systems. In: Novel catalyst materials for bioelectrochemical systems: fundamentals and applications. American Chemical Society, pp 45–71
9. Chakraborty I, Das S, Dubey BK, Ghangrekar MM (2020a) Novel low cost proton exchange membrane made from sulphonated biochar for application in microbial fuel cells. Mater Chem Phys 239:122025. https://doi.org/10.1016/j.matchemphys.2019.122025
10. Chakraborty I, Sathe SM, Dubey BK, Ghangrekar MM (2020b) Waste-derived biochar: applications and future perspective in microbial fuel cells. Bioresour Technol 312:123587. https://doi.org/10.1016/j.biortech.2020.123587
11. Cheraghipoor M, Mohebbi-Kalhori D, Noroozifar M, Maghsoodlou MT (2021) Production of greener energy in microbial fuel cell with ceramic separator fabricated using native soils: effect of lattice and porous SiO_2. Fuel 284:118938. https://doi.org/10.1016/j.fuel.2020.118938
12. Chouler J, Bentley I, Vaz F et al (2017) Exploring the use of cost-effective membrane materials for microbial fuel cell based sensors. Electrochim Acta 231:319–326. https://doi.org/10.1016/j.electacta.2017.01.195
13. Das I, Das S, Ghangrekar MM (2020a) Application of bimetallic low-cost CuZn as oxygen reduction cathode catalyst in lab-scale and field-scale microbial fuel cell. Chem Phys Lett 751:137536. https://doi.org/10.1016/j.cplett.2020.137536
14. Das I, Ghangrekar MM, Satyakam R et al (2020b) On-site sanitary wastewater treatment system using 720 L stacked microbial fuel cell: case study. J Hazard Toxic Radioact Waste 24:04020025. https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000518
15. Delord B, Neri W, Bertaux K et al (2017) Carbon nanotube fiber mats for microbial fuel cell electrodes. Bioresour Technol 243:1227–1231. https://doi.org/10.1016/j.biortech.2017.06.170
16. Ding W, Cheng S, Yu L, Huang H (2017) Effective swine wastewater treatment by combining microbial fuel cells with flocculation. Chemosphere 182:567–573. https://doi.org/10.1016/j.chemosphere.2017.05.006
17. Dong Y, Qu Y, He W et al (2015) A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode. Biores Technol 195:66–72. https://doi.org/10.1016/j.biortech.2015.06.026

18. Fangzhou D, Zhenglong L, Shaoqiang Y et al (2011) Electricity generation directly using human feces wastewater for life support system. Acta Astronautica 68:1537–1547. https://doi.org/10.1016/j.actaastro.2009.12.013Feng; Feng Y, He W, Liu J et al (2014) A horizontal plug flow and stackable pilot microbial fuel cell for municipal wastewater treatment. Bioresour Technol 156:132–138. https://doi.org/10.1016/j.biortech.2013.12.104
19. Gajda I, Greenman J, Ieropoulos IA (2018) Recent advancements in real-world microbial fuel cell applications. Curr Opin Electrochem 11:78–83. https://doi.org/10.1016/j.coelec.2018.09.006
20. Gajda I, Greenman J, Melhuish C, Ieropoulos I (2015) Self-sustainable electricity production from algae grown in a microbial fuel cell system. Biomass Bioenerg 82:87–93. https://doi.org/10.1016/j.biombioe.2015.05.017
21. Garita-Meza MA, Ramírez-Balderas LA, Contreras-Bustos R et al (2018) Blocking oscillator-based electronic circuit to harvest and boost the voltage produced by a compost-based microbial fuel cell stack. Sustain Energy Technol Assess 29:164–170. https://doi.org/10.1016/j.seta.2018.08.007
22. Ge Z, He Z (2016) Long-term performance of a 200 L modularized microbial fuel cell system treating municipal wastewater: treatment, energy, and cost. Environ Sci: Water Res Technol 2:274–281. https://doi.org/10.1039/C6EW00020G
23. Gil G-C, Chang I-S, Kim BH et al (2003) Operational parameters affecting the performannce of a mediator-less microbial fuel cell. Biosens Bioelectron 18:327–334. https://doi.org/10.1016/S0956-5663(02)00110-0
24. Greenman J, Ieropoulos IA (2017) Allometric scaling of microbial fuel cells and stacks: the lifeform case for scale-up. J Power Sour 356:365–370. https://doi.org/10.1016/j.jpowsour.2017.04.033
25. He W, Wallack MJ, Kim K-Y et al (2016) The effect of flow modes and electrode combinations on the performance of a multiple module microbial fuel cell installed at wastewater treatment plant. Water Res 105:351–360. https://doi.org/10.1016/j.watres.2016.09.008
26. He Z, Kan J, Mansfeld F et al (2009) Self-sustained phototrophic microbial fuel cells based on the synergistic cooperation between photosynthetic microorganisms and heterotrophic bacteria. Environ Sci Technol 43:1648–1654. https://doi.org/10.1021/es803084a
27. Hiegemann H, Herzer D, Nettmann E et al (2016) An integrated 45L pilot microbial fuel cell system at a full-scale wastewater treatment plant. Biores Technol 218:115–122. https://doi.org/10.1016/j.biortech.2016.06.052
28. Hiegemann H, Littfinski T, Krimmler S et al (2019) Performance and inorganic fouling of a submergible 255 L prototype microbial fuel cell module during continuous long-term operation with real municipal wastewater under practical conditions. Bioresour Technol 294:122227. https://doi.org/10.1016/j.biortech.2019.122227
29. Hill RA, Hunt J, Sanders E et al (2019) Effect of biochar on microbial growth: a metabolomics and bacteriological investigation in E. coli. Environ Sci Technol 53:2635–2646. https://doi.org/10.1021/acs.est.8b05024
30. Hou D, Lu L, Ren ZJ (2016) Microbial fuel cells and osmotic membrane bioreactors have mutual benefits for wastewater treatment and energy production. Water Res 98:183–189. https://doi.org/10.1016/j.watres.2016.04.017
31. Huggins T, Wang H, Kearns J et al (2014) Biochar as a sustainable electrode material for electricity production in microbial fuel cells. Biores Technol 157:114–119. https://doi.org/10.1016/j.biortech.2014.01.058
32. Huggins TM, Latorre A, Biffinger JC, Ren ZJ (2016) Biochar based microbial fuel cell for enhanced wastewater treatment and nutrient recovery. Sustainability 8:169. https://doi.org/10.3390/su8020169
33. Ichihashi O, Hirooka K (2012) Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. Biores Technol 114:303–307. https://doi.org/10.1016/j.biortech.2012.02.124
34. Ieropoulos I, Greenman J, Melhuish C (2010) Improved energy output levels from small-scale microbial fuel cells. Bioelectrochemistry 78:44–50. https://doi.org/10.1016/j.bioelechem.2009.05.009

35. Islam MA, Woon CW, Ethiraj B et al (2017) Ultrasound driven biofilm removal for stable power generation in microbial fuel cell. Energy Fuels 31:968–976. https://doi.org/10.1021/acs.energyfuels.6b02294
36. Jang JK, Kan J, Bretschger O et al (2013) Electricity generation by microbial fuel cell using microorganisms as catalyst in cathode 23:1765–1773. https://doi.org/10.4014/jmb.1310.10117
37. Jiang D, Curtis M, Troop E et al (2011) A pilot-scale study on utilizing multi-anode/cathode microbial fuel cells (MAC MFCs) to enhance the power production in wastewater treatment. Int J Hydrog Energy 36:876–884. https://doi.org/10.1016/j.ijhydene.2010.08.074
38. Jiang Y, Liang P, Zhang C et al (2015) Enhancing the response of microbial fuel cell based toxicity sensors to Cu(II) with the applying of flow-through electrodes and controlled anode potentials. Biores Technol 190:367–372. https://doi.org/10.1016/j.biortech.2015.04.127
39. Jin X, Yang N, Liu Y et al (2020) Bifunctional cathode using a biofilm and Pt/C catalyst for simultaneous electricity generation and nitrification in microbial fuel cells. Bioresour Technol 306:123120. https://doi.org/10.1016/j.biortech.2020.123120
40. Jonker JGG, Faaij APC (2013) Techno-economic assessment of micro-algae as feedstock for renewable bio-energy production. Appl Energy 102:461–475. https://doi.org/10.1016/j.apenergy.2012.07.053
41. Kalathil S, Lee J, Cho MH (2012) Efficient decolorization of real dye wastewater and bioelectricity generation using a novel single chamber biocathode-microbial fuel cell. Biores Technol 119:22–27. https://doi.org/10.1016/j.biortech.2012.05.059
42. Kalathil S, Patil SA, Pant D (2018) Microbial fuel cells: electrode materials. In: Wandelt K (ed) Encyclopedia of interfacial chemistry. Elsevier, Oxford, pp 309–318; Keller J, Rabaey K (2008) Experiences from MFC pilot plant operation: how to get the technology market-ready? In: Microbial fuel cells first international symposium 2008
43. Lefebvre O, Ooi WK, Tang Z et al (2009) Optimization of a Pt-free cathode suitable for practical applications of microbial fuel cells. Bioresour Technol 100:4907–4910. https://doi.org/10.1016/j.biortech.2009.04.061
44. Li H, He W, Qu Y et al (2017) Pilot-scale benthic microbial electrochemical system (BMES) for the bioremediation of polluted river sediment. J Power Sour 356:430–437. https://doi.org/10.1016/j.jpowsour.2017.03.066
45. Li T, Cai Y, Yang X-L et al (2020) Microbial fuel cell-membrane bioreactor integrated system for wastewater treatment and bioelectricity production: overview. J Environ Eng 146:04019092. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001608
46. Li W-W, Sheng G-P, Liu X-W, Yu H-Q (2011) Recent advances in the separators for microbial fuel cells. Biores Technol 102:244–252. https://doi.org/10.1016/j.biortech.2010.03.090
47. Li W-W, Yu H-Q, He Z (2014) Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. Energy Environ Sci 7:911–924. https://doi.org/10.1039/C3EE43106A
48. Liang P, Duan R, Jiang Y et al (2018) One-year operation of 1000 L modularized microbial fuel cell for municipal wastewater treatment. Water Res 141:1–8. https://doi.org/10.1016/j.watres.2018.04.066
49. Logan BE (2009) Exoelectrogenic bacteria that power microbial fuel cells. Nat Rev Microbiol 7:375–381. https://doi.org/10.1038/nrmicro2113
50. Lu M, Chen S, Babanova S et al (2017) Long-term performance of a 20 L continuous flow microbial fuel cell for treatment of brewery wastewater. J Power Sour 356:274–287. https://doi.org/10.1016/j.jpowsour.2017.03.132
51. Ma M, You S, Qu J, Ren N (2016) Natural eggshell membrane as separator for improved coulombic efficiency in air-cathode microbial fuel cells. RSC Adv 6:66147–66151. https://doi.org/10.1039/C6RA13052F
52. Mansoorian HJ, Mahvi AH, Jafari AJ, Khanjani N (2016) 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 20:88–100. https://doi.org/10.1016/j.jscs.2014.08.002

53. Mehravanfar H, Mahdavi MA, Gheshlaghi R (2019) Economic optimization of stacked microbial fuel cells to maximize power generation and treatment of wastewater with minimal operating costs. Int J Hydrog Energy 44:20355–20367. https://doi.org/10.1016/j.ijhydene.2019.06.010
54. Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM, Pant D (2019) A microbial fuel cell configured for the remediation of recalcitrant pollutants in soil environment. RSC Adv 9:41409–41418. https://doi.org/10.1039/C9RA06957G
55. Morris JM, Jin S (2007) Feasibility of using microbial fuel cell technology for bioremediation of hydrocarbons in groundwater. J Environ Sci Health Part A 43:18–23. https://doi.org/10.1080/10934520701750389
56. Myung J, Yang W, Saikaly PE, Logan BE (2018) Copper current collectors reduce long-term fouling of air cathodes in microbial fuel cells. Environ Sci: Water Res Technol 4:513–519. https://doi.org/10.1039/C7EW00518K
57. Namour P, Jobin L (2018) Electrochemistry, a tool to enhance self-purification in water systems while preventing the emission of noxious gases (greenhouse gases, H2S, NH3). Curr Opin Electrochem 11:25–33. https://doi.org/10.1016/j.coelec.2018.07.003
58. Nguyen C-L, Tartakovsky B, Woodward L (2019) Harvesting energy from multiple microbial fuel cells with a high-conversion efficiency power management system. ACS Omega 4:18978–18986. https://doi.org/10.1021/acsomega.9b01854
59. Oliot M, Etcheverry L, Mosdale A et al (2017) Separator electrode assembly (SEA) with 3-dimensional bioanode and removable air-cathode boosts microbial fuel cell performance. J Power Sour 356:389–399. https://doi.org/10.1016/j.jpowsour.2017.03.016
60. Oliot M, Etcheverry L, Mosdale R, Bergel A (2017) Microbial fuel cells connected in series in a common electrolyte underperform: understanding why and in what context such a set-up can be applied. Electrochim Acta 246:879–889. https://doi.org/10.1016/j.electacta.2017.06.114
61. Palanisamy G, Jung H-Y, Sadhasivam T et al (2019) A comprehensive review on microbial fuel cell technologies: processes, utilization, and advanced developments in electrodes and membranes. J Clean Prod 221:598–621. https://doi.org/10.1016/j.jclepro.2019.02.172
62. Pham TH, Aelterman P, Verstraete W (2009) Bioanode performance in bioelectrochemical systems: recent improvements and prospects. Trends Biotechnol 27:168–178. https://doi.org/10.1016/j.tibtech.2008.11.005
63. Pisciotta JM, Zaybak Z, Call DF et al (2012) Enrichment of microbial electrolysis cell biocathodes from sediment microbial fuel cell bioanodes. Appl Environ Microbiol 78:5212–5219. https://doi.org/10.1128/AEM.00480-12
64. Rossi R, Jones D, Myung J et al (2019) Evaluating a multi-panel air cathode through electrochemical and biotic tests. Water Res 148:51–59. https://doi.org/10.1016/j.watres.2018.10.022
65. Rossi R, Yang W, Zikmund E et al (2018) In situ biofilm removal from air cathodes in microbial fuel cells treating domestic wastewater. Biores Technol 265:200–206. https://doi.org/10.1016/j.biortech.2018.06.008
66. Rozendal RA, Hamelers HVM, Buisman CJN (2006) Effects of membrane cation transport on pH and microbial fuel cell performance. Environ Sci Technol 40:5206–5211. https://doi.org/10.1021/es060387r
67. Senthilkumar N, Pannipara M, Al-Sehemi AG, Kumar GG (2019) PEDOT/NiFe2O4 nanocomposites on biochar as a free-standing anode for high-performance and durable microbial fuel cells. New J Chem 43:7743–7750. https://doi.org/10.1039/C9NJ00638A
68. Sivasankar P, Poongodi S, Seedevi P et al (2019) Bioremediation of wastewater through a quorum sensing triggered MFC: a sustainable measure for waste to energy concept. J Environ Manag 237:84–93. https://doi.org/10.1016/j.jenvman.2019.01.075
69. Sonawane JM, Patil SA, Ghosh PC, Adeloju SB (2018) Low-cost stainless-steel wool anodes modified with polyaniline and polypyrrole for high-performance microbial fuel cells. J Power Sour 379:103–114. https://doi.org/10.1016/j.jpowsour.2018.01.001
70. Tabassum N, Islam N, Ahmed S (2021) Progress in microbial fuel cells for sustainable management of industrial effluents. Process Biochem 106:20–41. https://doi.org/10.1016/j.procbio.2021.03.032

71. Tang C, Zhao Y, Kang C et al (2019) Towards concurrent pollutants removal and high energy harvesting in a pilot-scale CW-MFC: insight into the cathode conditions and electrodes connection. Chem Eng J 373:150–160. https://doi.org/10.1016/j.cej.2019.05.035
72. Tremouli A, Greenman J, Ieropoulos I (2018) Investigation of ceramic MFC stacks for urine energy extraction. Bioelectrochemistry 123:19–25. https://doi.org/10.1016/j.bioelechem.2018.03.010
73. Vilajeliu-Pons A, Puig S, Salcedo-Dávila I et al (2017) Long-term assessment of six-stacked scaled-up MFCs treating swine manure with different electrode materials. Environ Sci: Water Res Technol 3:947–959. https://doi.org/10.1039/C7EW00079K
74. Walter XA, Gajda I, Forbes S et al (2016) Scaling-up of a novel, simplified MFC stack based on a self-stratifying urine column. Biotechnol Biofuels 9. https://doi.org/10.1186/s13068-016-0504-3
75. Wang C-T, Sangeetha T, Ding D-Q et al (2018) Implementation of surface modified carbon cloth electrodes with biochar particles in microbial fuel cells. Int J Green Energy 15:789–794. https://doi.org/10.1080/15435075.2018.1529576
76. Wang H, Yi S, Cao X et al (2017) Reductive dechlorination of hexachlorobenzene subjected to several conditions in a bioelectrochemical system. Ecotoxicol Environ Saf 139:172–178. https://doi.org/10.1016/j.ecoenv.2017.01.039
77. Wang X, Feng Y, Wang H et al (2009) Bioaugmentation for electricity generation from corn stover biomass using microbial fuel cells. Environ Sci Technol 43:6088–6093. https://doi.org/10.1021/es900391b
78. Watanabe T, Jin H-W, Cho K-J, Kuroda M (2005) Direct treatment of an acidic and high-strength nitrate-polluted wastewater containing heavy metals by using a bio-electrochemical reactor. Dev Chem Eng Miner Process 13:627–638. https://doi.org/10.1002/apj.5500130512
79. Wu G, Bao H, Xia Z et al (2018) Polypyrrole/sargassum activated carbon modified stainless-steel sponge as high-performance and low-cost bioanode for microbial fuel cells. J Power Sour 384:86–92. https://doi.org/10.1016/j.jpowsour.2018.02.045
80. Wu S, Li H, Zhou X et al (2016) A novel pilot-scale stacked microbial fuel cell for efficient electricity generation and wastewater treatment. Water Res 98:396–403. https://doi.org/10.1016/j.watres.2016.04.043
81. Wu X, Zhu X, Song T et al (2015) Effect of acclimatization on hexavalent chromium reduction in a biocathode microbial fuel cell. Biores Technol 180:185–191. https://doi.org/10.1016/j.biortech.2014.12.105
82. Xu J, Sheng G-P, Luo H-W et al (2012) Fouling of proton exchange membrane (PEM) deteriorates the performance of microbial fuel cell. Water Res 46:1817–1824. https://doi.org/10.1016/j.watres.2011.12.060
83. Yang W, Rossi R, Tian Y et al (2018) Mitigating external and internal cathode fouling using a polymer bonded separator in microbial fuel cells. Biores Technol 249:1080–1084. https://doi.org/10.1016/j.biortech.2017.10.109
84. Yang W, Watson VJ, Logan BE (2016) Substantial humic acid adsorption to activated carbon air cathodes produces a small reduction in catalytic activity. Environ Sci Technol 50:8904–8909. https://doi.org/10.1021/acs.est.6b00827
85. Ye Y, Ngo HH, Guo W et al (2019) Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater. Chem Eng J 358:236–242. https://doi.org/10.1016/j.cej.2018.09.215
86. Yousefi V, Mohebbi-Kalhori D, Samimi A (2017) Ceramic-based microbial fuel cells (MFCs): a review. Int J Hydrog Energy 42:1672–1690. https://doi.org/10.1016/j.ijhydene.2016.06.054
87. Yuan Y, Liu T, Fu P et al (2015) Conversion of sewage sludge into high-performance bifunctional electrode materials for microbial energy harvesting. J Mater Chem A 3:8475–8482. https://doi.org/10.1039/C5TA00458F
88. Yuan Y, Yuan T, Wang D et al (2013) Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in an microbial fuel cell. Biores Technol 144:115–120. https://doi.org/10.1016/j.biortech.2013.06.075

89. Zhang C (2019) Effects of scale-up. Nat Energy 4:6–6. https://doi.org/10.1038/s41560-018-0319-5
90. Zhang E, Wang F, Yu Q et al (2017) Durability and regeneration of activated carbon air-cathodes in long-term operated microbial fuel cells. J Power Sour 360:21–27. https://doi.org/10.1016/j.jpowsour.2017.05.119
91. Zhang F, He Z (2012) Simultaneous nitrification and denitrification with electricity generation in dual-cathode microbial fuel cells. J Chem Technol Biotechnol 87:153–159. https://doi.org/10.1002/jctb.2700
92. Zhao H, Zhao J, Li F, Li X (2016) Performance of denitrifying microbial fuel cell with biocathode over nitrite. Front Microbiol 7:344. https://doi.org/10.3389/fmicb.2016.00344
93. Zhao Y, Nakanishi S, Watanabe K, Hashimoto K (2011) Hydroxylated and aminated polyaniline nanowire networks for improving anode performance in microbial fuel cells. J Biosci Bioeng 112:63–66. https://doi.org/10.1016/j.jbiosc.2011.03.014
94. Zhuang L, Yuan Y, Wang Y, Zhou S (2012) Long-term evaluation of a 10 L serpentine-type microbial fuel cell stack treating brewery wastewater. Biores Technol 123:406–412. https://doi.org/10.1016/j.biortech.2012.07.038
95. Zhuang L, Zhou S (2009) Substrate cross-conduction effect on the performance of serially connected microbial fuel cell stack. Electrochem Commun 11:937–940. https://doi.org/10.1016/j.elecom.2009.02.027
96. Zhuang L, Zhou S, Li Y, Yuan Y (2010) Enhanced performance of air-cathode two-chamber microbial fuel cells with high-pH anode and low-pH cathode. Biores Technol 101:3514–3519. https://doi.org/10.1016/j.biortech.2009.12.105

Conventional Electrode Materials for Microbial Fuel Cells

Rabia Tasaduq Hussain, Khalid Umar, Akil Ahmad, Showkat Ahmad Bhawani, and Mohammed B. Alshammari

Abstract The use of microbial fuel cells (MFCs) has gained a lot of attention as a means to combat both energy shortages and water pollution. Despite their best efforts, MFCs are unable to produce substantial amounts of energy or effectively remove pollutants due to a number of difficulties, one of which being the electrode. One of the most significant components of an MFC is the electrode. Different types of electrode materials have recently been developed to boost pollutant removal rates and energy production efficiency. Carbon-based materials have been used as the most often used electrode material in MFCs. A wide range of potentials is now accessible for use in the manufacturing of electrode materials, which can significantly reduce current issues such as the demand for high-quality materials and their cost. In the present chapter, the conventional electrode material is briefly discussed with their influence and role in MFC operation and performance. A brief discussion of the current issues and future views of electrode materials is also included.

Keywords Microbial fuel cells · Electrode material · Biomass · Energy generation

R. T. Hussain · K. Umar
School of Chemical Sciences, Universiti Sains Malaysia (USM), 11800 George Town, Penang, Malaysia

A. Ahmad (✉) · M. B. Alshammari
Chemistry Department, College of Sciences and Humanities, Prince Sattam Bin Abdulaziz University, Al-Kharj, Saudi Arabia
e-mail: aj.ahmad@psau.edu.sa

M. B. Alshammari
e-mail: m.alshammari@psau.edu.sa

S. A. Bhawani
Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS), 94300 Kota Samarahan, Malaysia

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_6

1 Introduction

An eco-friendly and green environment is one of the necessities for human beings to live a healthy life, but due to discharge of industrial effluents containing irorganic and organic pollutants into water bodies, results in water contamination which has adverse effects on human beings and other aquatic life [1–3]. These crises are well countered by the microbial fuel cell approach due to its unique properties of achieving energy and wastewater treatments [4]. The microbial fuel cells (MFCs) approach is an innovative step in research to convert toxic chemicals into non-toxic chemicals and convert chemical outputs to electrical outputs in the form of energies by using various catalysts (e.g., bacteria) present in wastewater [5, 6]. There have been significant advancements in wastewater remediations and power outputs. MFCs have yet to be commercialized due to their low energy generation and removal efficiency. Low energy consumption or removal efficiency can be caused by a variety of factors, including the utilization of low-graded materials as working electrodes or material cost issues. Because it offers the essential surface area for bacterial proliferation, the working electrode seems to be the most critical section of MFCs. These bacteria produce electrons and protons and transferred it to the anode. Fabrication of anode materials for MFCs functioning, on the other hand, remains difficult. Recently, there has been a surge of interest in electrode configurations, materials, and design that results in steadily increased performance of MFCs [7]. Electrode grading materials should have a few general features to face high-performance criteria, including high conductivity, comparable biocompatibility, stable thermal temperature, chemical and electrical stability, mechanical strength, and an expanded surface region. MFCs use a variety of electrode graded materials, however, these graded materials have several limitations that are unsuitable for industrial usage [2, 8]. According to a prior study, electrode modification has emerged as a novel point in the field of MFCs for achieving an expansion of surface regions, bacterial adherence, and have the ability of electron transference

In MFCs, the electrode is known as the cathode and anode in which anode plays a vital role to transfer bacteria toward cathode to generate electricity. The materials used in the fabrication of anodes have some limitations and till now, not applied at large scale. In literature, El Mekawy [9] et al. mention that anode is the crucial part of MFCs fabrication approaches. As in our knowledge that many researchers started their study on graphene derivatives as modifiers or enhancers to provide a good performance of MFCs on electrode surfaces either as anode or cathode. From one of the previous reports [9], the authors come to the conclusion that graphene derivatives based or carbon-based materials electrodes as cathode or anode are shown as superior and emerging materials for electrodes in MFCs. These materials provide a new dimensions to the researchers working in same area due to cost-effective and efficient materials [10]. Nowadays, the most usable graphene derivative, graphene oxide, is easily fabricated through industrial and domestic waste materials. Moreover, the issue of corrosion or the influence of toxic bacteria on MFCs is resolved by

using polymer layers or metal oxide layers with graphene derivatives. The modifications of polymers and metallic composites not only resolved the corrosion issues, but also increase the working performance and efficiency of the electrode in MFCs [11, 12]. It increased the conductivity, biocompatibility, and stability between bacteria and electrodes either as anode or cathode. That's why it is an up-to-date approach to modify electrodes with graphene or carbon-based derivatives to achieve better performance. In this chapter, we reviewed the different types of electrode materials with their unique properties of surface modifications, sizes, designs, electricity generation, and inoculation sources. To discuss the significance of biomass wastes as an emerging materials, many ideas and sources based on electrode fabrications have been summarized in this chapter. Furthermore, the effects of electrodes on wastewater remediation and energy processing are discussed, together with new difficulties and prospects.

2 Essential Properties of Electrode Materials

It is foremost and essential step in MFCs to investigate the unique properties of electrode materials in terms of achieving steady electron mobility, electrochemical efficiency, and bacterial adhesions between system and electrode materials [13]. Some of the unique properties which helps us in this matter is mentioned in this chapter to understand the reproducibility of working of MFCs.

2.1 Conductivity of Material

It is an important aspect of electrode because the electrons due to bacterial adhesions travel from negative terminal to positive terminal via the channel of outer circuit. As in literature, the electrode material is in charge of allowing electrons to flow and enhance their speed [14, 15]. The more highly conductive materials are more helpful in resisting the bulk solutions resistance and increasing the electron transfer rate [16]. To improve electron transfer, lower the interfacial impedance between substrate and electrode as mentioned in the literature [17, 18]. Before constructing the electrodes for MFCs, the electrical conductivity of materials is typically investigated.

2.2 Physiological Properties

The surface regions of the electrode severely affects energy generation in MFCs [19–21]. Because resistivity of electrodes depends on ohmic losses in a MFCs, increasing

its surface area is the given suggestions in reports to minimize resistance power. More active sites are gained with an expanded surface regions for bacterial colonization and improves the efficiency of the electrode kinetics. Microorganisms, for example, *Geobacter species, E. coli, Pseudomonas species*, and others were immobilized efficiently on the active regions of electrodes, allowing for suitable electron transfer [20]. Because biological responses occur on the active regions of the electrodes, the surface regions has a significant impact on MFC performance [22].

2.3 Material Biocompatibility

The anode electrode's biocompatibility is critical in MFC operations since it comes into direct contact with microscopic organisms and their respiration cycles. Many materials utilized as electrodes in MFCs, such as silver, gold, and copper, are not considered biocompatible due to their corrosive nature [23–25]. The poisonous nature of such compounds can prevent bacterial development during MFC operation, resulting in lower energy generation.

2.4 Stability and Durability

In case of any research-based system, the stability and durability are one of the most significant points for your research. Various environmental factors affect the stability and durability of electrode. The decomposition, corrosion, and swelling are caused due to interaction of electrode with environment that affects its stability and duration of working performance [23, 26, 27]. Thus, the use of more preferable material as an electrode makes your system more durable and stable for good performance.

2.5 Cost and Access of Material

The cost and access of material is a key factor to approach your work without stress and also opens the feasible ways for other researchers. And moreover, the cost of electrode also has chance to provide MFCs system with easy and cheap approach as compared to expensive and heavy approaches. In present time, carbon derived graphene based composites have been widely used due to easily available and low cost. The expensive metal composites such as gold, silver, platinum are also replaced with inexpensive bimetal composites such as ZnO, Fe_2O_3, etc. [28, 29].

3 Electrode Materials

Removal efficiency of pollutants and energy production have been optimized to investigate the effectiveness of electrode materials. The electrode materials, as mentioned above, has some of the basic properties such as high stability and conductivity, more compatible than other materials. For this purpose, we investigated some electrode materials in two categories as electrode material as anode and electrode material as cathode.

3.1 Electrode Materials as Anode

From previous studies, it becomes clear that there are various types of materials used to fabricate anode of MFCs in terms of large surface area to increase the extracellular efficiency of electron transfer via biofilm. Moreover, the anode materials have more significancy because it is useful for metabolic rates in oxidizing organic wastes by anaerobic microorganisms [30–32]. It is notable that the kinds and concentration of bacteria have great effect on power density of MFCs, but now, it is also proven that the anode materials have also significant feature for MFCs to work better. Thus, fabrication of the anode materials through various chemical modifications, must be taken an account in the future to enhance the capacity of anode. Some of the generally used sources are composite materials, allotropes of carbon, conducting polymers, or metal or metal oxides, which seem to have significant value to be worth materials for anode fabrication.

3.2 Carbon-Graded Materials

Nowadays, carbon-derived materials are gaining more attention due to their unique properties such as low cost, chemical and mechanical stability, high electron transfer kinetics, biocompatibility, and highly conductive in nature. By studying the recent literature, it is well known that different types of carbon-graded materials like graphite, carbon nanotubes, fullerenes, carbon nanorods, carbon cloth paper, carbon fiber, reticulated vitreous carbon, glassy carbon, and carbon quantum dots have been investigated. The latest carbon-based materials which are now an emerging class of carbon allotropes are graphene and its derivatives.

Carbon paper, brushes, rods, felt, fabric, meshes, and other carbon-graded materials are normally utilized materials in MFCs. A carbon mesh is somewhat more affordable than other carbon structures, as indicated by Wang et al. [33] and it likewise has a higher current thickness. On the other hand, modification of carbon meshes with alkali or gas give good results. Therefore, no untreated material presently

conveys a more powerful thickness. Borsje et al. [34] investigated the functioning of single carbon granules as capacitive bioanodes. Charge stockpiling execution and current creation via solitary carbon granule was utilized to decide the outcomes. The bioanode stored the charge in the form of two-fold sandwich. To assess the undiscovered capability of granular bioanodes, scientists utilized granular and initiated graphite carbon granules. In contrast with Ag/AgCl anodes, single enacted carbon-graded granules create 0.6 mA at 300 mV. Capacitive granules produce 1.3 times extra electricity as compared to graphite granules at the lower surface regions [35–37]. Li et al. [38] investigated granule-activated carbon, which delivered twice more energy than the customary carbon materials. According to the findings, granule-actuated carbon could be a viable alternative for anode preparation. Carbon cloth/sheets are flexible and allow bacteria to grow on their surface. It is, however, much more expensive at larger scales [39]. Actuated carbon cloth has an expanded surface region and suitable adsorption capacity for the expulsion of sulphide in electrochemical oxidation at the anode. Wang et al. [40] arranged carbon cloth that provides an increment of the current effectiveness of 2777.7 mW/m^2. Doped with nitrogen gas, the carbon cloth produced high power production, and it could be valuable for future researches. Likewise, graphite is one of the regular forms utilized for an electrode in MFCs. Graphite is known as a crystalline allotrope of carbon with Sp^2 hybridization. MFCs use graphite as an anode because of its good conductivity and long-term stability. For the production of electrodes, different forms of graphite are effectively used [41–43]. Ter-Heijne et al. [44] observed the raw form of carbon for the electrode in MFC rather than flat forms, which showed higher current density. But they have a low surface region and high cost which makes this material inadequate for commercial use in the production of energy. The graphite brush as the best model for electrodes with the best performance to be used as anodes in MRCs for improved energy generation and toxic pollution removal was reported by Lowy et al. [45]. Yazdi et al. [46] later reported that the rate of bacterial colonization on the electrode's surface is proportional to the anode's surface area. In another study, Zhang et al. [47] found a category of graphite brushes within the range of sizes. Little brushes can deliver more energy output than bigger ones. 1771 mW/m^2 small value of power density is also reported in the Cassava mill by graphitic brushes in wastewater remediation [48, 49]. Bacteria feed on organic material and flourish in environments with lots of carbon because of its increased particular surface area [50]. Yasri et al. [51] created an efficient anode material by doping graphite with calcium sulphide to promote bacterial interaction with the active regions of electrodes. In the modern period, graphene, a newly developing carbon allotrope (found in a 2D hexagonal lattice), has earned a lot of interest. With its emerging features of outstanding conductivity and mechanical and thermal strength, graphene is an ideal material for electrode construction. When compared to graphite materials, graphene possesses a nonlinear and better diamagnetism. Graphene and its derivatives, on the other hand, are still being studied as anodes in MFCs [52]. Graphene has been synthesized using a variety of processes. Commercially available graphene is expensive, whereas graphene made from waste materials is less expensive [53–56] Due to its more energy generation relative to other typical carbons, graphene as an anodic material enables high scale functioning

for MFCs. Graphene-based electrodes have better electrode efficiency as anodes than conventional carbon-based electrodes [57]. During MFC operations, graphene has non-toxic impacts on bacterial growth. As a result, by modifying or combining it with conductive polymers and metals, drawbacks of other materials, like copper, can be reduced [58, 59]. Modified carbon allotropes have the potential to revolutionize wastewater treatment and energy.

3.3 Natural Biomass Source as Anode

The properties of the electrode materials vary significantly in terms of physical, chemical, and biological nature. The electrodes require electrical, and specifically microbial, compatibility with specific bacteria strains to affect the movement of electrons, just as surface opposition of electrodes [60]. Nonetheless, electrode materials, fabrication, and processing have been recently becoming a popular and up-and-coming research area. MFCs use waste materials for construction. Changing waste materials into worthy and valuable materials is time-consuming and somehow effective in contrast with commercial materials in a few features [61]. Cheng et al. [62] researched a waste-inferred decreased graphene (rGO) composite for anodes to accomplish more powerful outcomes as far as energy age and wastewater treatment by means of MFCs. Utilizing dried eucalyptus leaves as waste material, the rGO was prepared successfully. Later, rGO/gold nanoparticle nanocomposites were fabricated by layering for the manufacturing of biocompatible anodes. The electrode prepared in this study has a higher surface roughness, which facilitates bacterial colonization. Gold nanoparticles are considered as a highly electroactive agent which tranfer the electrons and produces electricity at negative terminal. Singh et al. [63] prepared an effective electrode for MFCs using carbon nanoparticles derived from candle soot. The candle sediment was disseminated on the outer layer of a hardened steel circle, which permitted the carbon nanoparticles to be utilized as cathodes straightforwardly. The consequences of the electrical, physical, and compound portrayal of an anode's mechanical, chemical and electrical strength are just as progressively permeable qualities. The production of carbon nanoparticle electrodes from candle soot is reusable, budget-friendly, robust, and dependable. Bose et al. [64] have also used biomass to manufacture a bioenergy active carbon cathode via MFCs. This was one of a kind method of generating electricity and treating water that had no negative environmental consequences. Platinum is commonly utilized as an impetus for oxygen decrease at the terminal of the cathode. In terms of reliability, functionality, and prices, the authors examined the effectiveness of actuated carbon derived from sugar cane waste. At different temperatures for 60 min, this useless material followed the carbonization process. Electrodes derived from various biomass sources are considered as an alternative for the treatment of pollutants from wastewater with electricity generation simultaneously. As we know that in MFCs, there have been

only a small number of publications on the source of biomass anodes. That's why the concept of reusability of biomass is a viable substitute for enhancing MFC's working efficiency with no high costs. Graphene and its derivatives can easily be produced by numerous methods like chemical vapor deposition, arc detection, epitaxial growth, scotch tape, electrochemical synthesis, reduction of GO/rGO, exfoliation, confined self-assembly, and Hummer's method. Its favorable points over other methods made it the most important and promising method. This is an eco-friendly method, for example, without producing harmful gases during processing, with a structured product, and with a larger output supplied. Hung et al. recently used [65] a coffee-based renewable waste anode in MFCs to expand the power thickness. The authors have transformed waste material into precious carbonized materials and have used it to lessen squander from the environment as an anodic material in MFC. The energy density achieved was 3800 mW/m^2, much higher than traditional techniques. In our vicinity, various types of waste materials cause serious dangers. Therefore, the use of biomass waste materials as valuable materials is a positive approach. In Hummer's process, however, various useless materials are carbonized to obtain fine carbonated powder materials affected by argon gas at 1050 °C. The graphic powder is treated to obtain graphene oxide with the oxidizing agent $KMnO_4/H_2O_2$. Fabricated graphene oxide can also be used to manufacture the graphene oxide material in anode-shaped electrodes with polymer binders like nafion, polyethyleneimine, and polylactic acid [66]. The graphene oxide synthesized can be utilized as positive or negative terminal material, however, its use as the anode is preferable, as previously stated. This type of modification may enhance the materials efficiency and reduces the expenses. The use of composites synthesized for low-cost use with metal oxides such as CuO/GO, ZnO/GO, etc., is an optimal way to deal with various difficulties. Table 1 summarizes the electrodes produced in recent years using natural biomass resources.

3.4 Metal/metal Oxide-Sourced Materials

Different materials were utilized to fabricate metal/metal oxides based anode–cathode, but consumption restricts the utilization of metal-sourced terminals, especially for MFC anodes. Metals are commonly penetrable than carbon-graded materials because of their capacity to work with proficient electron stream [76]. While each metal has exceptional properties, not all metals are reasonable for cathode creation because of the noncorrosive necessities of the interaction. Also, certain metals repress bacterial bonds. For instance, in contrast with other carbon-graded materials, for example, graphite and graphene, non-destructive tempered steel materials don't have a powerful thickness. Overall, the smooth surfaces of metals are not helpful for bacterial grip. Predefined non-destructive materials, like tempered steel, can't accomplish higher energy thickness than materials dependent on carbon. At the

Table 1 List of electrodes synthesized using natural waste resource for MFCs

Electrode materials	Inoculum sources	Surface area of electrodes (cm^2)	Power density (mW/m^2)	Size of electrodes (cm^2)	References
Loofah sponge/PANI	Mix sludge	10.99	2590	0.5 × 3.0	Tang et al. [67]
Barbed chestnut shell	Mix sludge	91	759	2.7 × 2.7	Chen et al. [68]
Coconut shell/ sewage sludge	Mix sludge	10.99	1069	0.5 × 3.0	Yuan et al. [69]
Onion peels	Mix sludge	7	742	1.0 × 2.0 × 0.5	Li et al. [70]
Silk cocoon	Mix sludge	7	5	–	Li et al. [71]
Coffee wastes	Domestic waste	1	3927	–	Hung et al. [65]
Loofah sponge	Anaerobic sludge	10.99	701	0.5 × 3.0	Tang et al. [72]
Compressed milling residue	Anaerobic mix sludge	10.99	532	0.5 × 3.0	Huggins et al. [73]
Bamboo charcoal	Anaerobic mix sludge	59.21	1652	2.4 × 1.57	Zhang et al. [74]
Kenaf	Domestic sewage	2.5	–	0.23 × 1.52	Chen et al. [75]
Chestnut shells	Anaerobic mix sludge	125.65	850	0.3 × 66.4	Cheng et al. [62]

anode chamber, stainless steel had a power density of 23 mW/m^2 [77]. An anode-based stainless-steel grid increased the relative current density of a single electrode of graphite [78, 79]. Silver, platinum, gold, and titanium are ideal anode metals. While noble metal-based anode electrodes contribute to the reduction of interior obstruction in MFCs, their significant expense and poor bacterial grip block their far and widespread use in MFC operation [24, 80]. Platinum and titanium are commonly suitable as catalysts to enhance electrode performance [81]. Moreover, commercialization of some of pure metal-based anodes in MFCs have some limitation due to their high expense. The reactivity of metallic nanoparticles and transition metals is comparable to precious metals, altogether decreasing obstruction and working on microscopic organisms' connection to surfaces. Additionally, nanometallic particles offer an excellent opportunity to diminish the impact of harmfulness on bacterial cells [82]. These issues are mitigated by coating metal/metal oxide nanoparticles (Ag, ZnO, etc.) with comparable materials such as carbon-graded or polymers.

3.5 Polymer Composite Material

Various conductive polymers, namely polypyyrole, polyindoles, polythiophene, polycarbazoles, polyaniline, polyadenines, etc., were used in terms of highly conductive materials at anode surfaces on the basis of their efficient conductive properties [83–85]. The combination of carbon-based materials and conductive polymers produce very efficient and good results. As shown in previous reports, the polyaniline-modified carbon cloth produced more power production than unmodified carbon cloth [86]. In another report, one of the most important conductive polymers, polypyyrole with the layer of carbon paper, showed a 452 mW/m^2 power output [87]. To our knowledge, Polypyyrole can enter bacterial cell membranes and transport electrons via metabolic pathway easily [88]. Thus, polymer composites combined with different materials, similar to carbon-graded materials and metals, significantly further develop anode productivity. For example, Dumitru et al. [89] investigated two polymers such as polypyyrole and polyaniline with CNTs as a nanocomposite anode. Due to their synergistic effect, CNTs and conducting polymer nanocomposites perform justifiably well enough in electrochemical applications [90]. The use of conductive polymers (especially polyaniline and polycarbazole) with metal oxide composites could significantly improve MFC performance [91–93] But despite more researches, there is little exertion that has been made to plan polymeric composite-based MFC electrodes. Figure 1 depicts common electrodes such as conductive polymer, metal, and carbon electrodes.

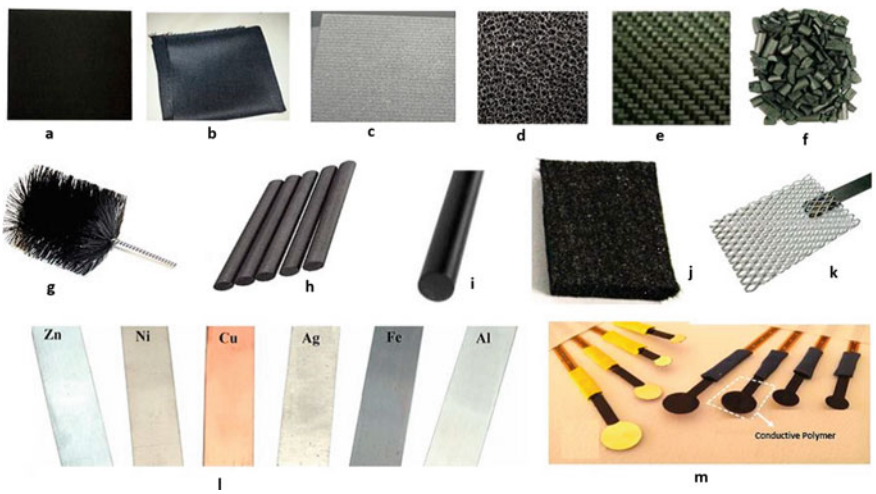

Fig. 1 List of commonly used electrodes: **a** carbon paper, **b** carbon cloth, **c** carbon fiber, **d** reticulated vitrified carbon, **e** carbon mesh, **f** graphitic granular, **g** carbon brushes, **h** graphite rod, **i** polycrystalline graphite, **j** carbon felt, **k** platinum mesh, **l** different metal electrode strips, and **m** conductive polymer-based strips. Adapted from reference [25] with MDPI permission

4 Electrode Materials as Cathode

Despite the anode (negative terminal), the cathode (positive terminal) material has also a significant place in the functioning of MFCs. Nowadays, the most widespread material for the cathode is carbon-based, but their features like size, model, and efficiency for cathode materials are challenging as compared to anode material [94–97]. The mostly reported anode materials are also used as cathode material. Due to deprived catalyst activity, reactions to reduce substrate commonly occur in the cathode section, reducing MFC performance [98–101]. The cathode terminals can be derived as with catalyst or without catalyst. The main distinction between these setups is the spark. Platinum and titanium are the most commonly used catalysts. A terminal named air cathode is directly influenced by oxygen [102]. The setup has drawn attention for its lack of aeration, functional simplicity, and appropriate electrode design. An air cathode can significantly expand the energy effectiveness through MFCs [103, 104]. Aqueous air cathodes use conductive materials like platinum meshes and carbon felt, cloth, and fiber to form electrodes. The catalyst is sandwiched with aqueous regions in low oxygen contact [105]. As an air cathode, carbon-derived forms are the most ideal conductive material. Catalysts (platinum, copper, etc.) are fixed to electrodes using binders [106, 107]. Poly(tetrafluoroethylene) and perfluorosulfonic acid are popular binders (nafion). Zhang et al. [108] compared the performance of articulated carbon and its derivatives as cathode utilizing poly(tetrafluoroethylene) for binding. In the presence of Pt as a catalyst, articulated carbon outperforms carbon cloth (1220 mW/m^2) in terms of power density. So articulated carbon seems to be a good cathode material substitute for the fabrication of a positive terminal. Zhao et al. [109] employed catalyst Pt combined carbon derived as a motivating factor. According to the latest findings, this catalyst has a power efficiency of 1.2 W/m^3. Cu is a preferable catalyst to Pt at lower temperatures due to its sustainable power. Under normal conditions, Pt is considered better and more generally known catalyst than other metals [110]. As a result, the materials utilized in the fabrication of positive and negative terminals (cathode/anode) can be performed as oxygen reduction catalysts. Due to their low overpotential, gold and platinum are considered potential catalysts, but their expensive cost makes them unsuitable [76, 111, 112]. Transition metals are cosidered as a alternative materials to fabricate potential electrode due to high stability, affordable and avoid any disruption in the microbial fuel system. Composite materials, known as molybdenum and carbide, perform well, but stainless steel and nickel alloys outperform them all [113]. Nanocomposites, on the other hand, are less expensive and provide a significant chance to boost MFC efficiency (for example, Ni and palladium nanoparticles/nanomaterials) [114]. In comparison to conventional materials, nanomaterials have an expanded surface region, superior electrochemical functioning, and stronger thermal and mechanical durability [115]. To improve the oxygen reduction reaction, a recent trend involves modifying the electrode using additional materials. According to the literature, fresh materials must be studied in order to improve the feasibility of electrodes, particularly anodes. Utilization of high-graded materials for anodes, for example, graphene and its derivatives with metal

oxides, could usher in a major shift in the MFC area. The preferable composites are GO/Ag, GO/Fe_2O_3, GO/ZnO, GO/chitosan, and GO/TiO_2, all of which have a significant influence on power outputs. In addition, Table 2 lists the many types of classic carbon-graded materials, composite-based, metal/metal oxides, and Carbon-based + Polymer composite that can be utilized as electrodes (anodes and cathodes).

5 Influence of Electrodes (Cathode/Anode/) in MFCs

In the presence of a biocatalyst, the electrode (anode/cathode) is a critical component due to its unique feature of assisting in the remediation of hazardous agents and generation of energy during MFC operations. During the respiration process of bacteria, the bacteria are cooperated with the electrode region to create protons and electrons. As seen in Fig. 2, the electrode provides enough surface region for bacteria to proliferate and oxidize. The performance of the anode as compared to the cathode provides MFCs with high electric production, wastewater bioremediation, and compactable economic features.

6 Influence of Electrode (Anode/Cathode) on Removal of Pollutants

MFCs are thought to be a particularly efficient prospective use for wastewater bioremediation. Many traditional wastewater treatment technologies have been described, but they all have significant limitations such as high prices, being difficult to run, the possibility of self-toxicity, and being unstable in terms of ecosystem safety [51]. Fossil fuel industrial wastewater, scum wastewater, aquaculture wastewater, cassava mill wastewater, food processing waste, dairy wastewater, crop residues, and surgical cotton waste, are all examples of wastewater that could benefit from the MFC approach [151]. Organic agents are oxidized to generate electrons and protons in the chamber of the anode via exoelectrogens, thereby destroying the hazardous organic pollutants in water [152, 153]. Protons were transmitted directly to the cathode or via membrane sources, while electrons were transported via the outer circuit. The electrodes' functioning efficiency is crucial to this procedure. The electrodes offer bacteria a surface area for respiration and growth, making it easier for electrons and protons to be transferred to the negative chamber through bacteria and ultimately to the positive chamber.

Zhang et al. [154] investigated the suppression of two elements with the implementation of electricity utilizing vanadium-sourced water with waste as an electron acceptor in dual terminal microbial fuel cells. V(V) and Cr (VI) are primary metals found in vanadium-sourced effluent, both of which are highly hazardous and abundant. Qiu et al. [155] reported vanadium based biocathode and got 60% fatality rate

Table 2 Some reported materials used as electrodes in microbial fuel cells

Type of materials	Anode	Cathode	Catalyst	Power density	Inoculum source/bacteria	References
Carbon-based	Carbon mesh	Carbon mesh	Pt	893 mW/m^2	Pre-acclimated bacteria from an active MFC	Wang et al. [116]
Carbon-based	Activated carbon cloth	Graphite foil	Pt	0.51 mW/cm^2	D desulfuricans strain	Sokol and Bradford [37]
Carbon-based	Non-wet proofed carbon cloth	Wet proofed carbon cloth	Pt	766 mW/m^2	Domestic wastewater	Cheng et al. [117]
Carbon-based	Plain carbon paper	Carbon paper	Pt	33 mW/m^2	Sediment sludge	Logan et al. [118]
Carbon-based	Granular graphite	Granular graphite	Pt	8 W/m^3	Mixture of sediment, aerobic and anaerobic sludge	Clauwaert et al. [119]
Carbon-based	Granular graphite	Graphite felts	Pt	83 $\pm$ 11 W/m^3	Mixture of sediment, aerobic and anaerobic sludge	Clauwaert et al. [120]
Carbon-based	Graphite plate	Graphite fiber brushes	Pt	68.4 W/m^3	Aerobic sludge	You et al. [121]
Carbon-based	Carbon cloth	Carbon cloth	Without catalyst	679.7 mW/m^2	*S.putrefaciens CN32*	Qiao et al. [122]
Carbon-based	Carbon cloth	Carbon cloth	Without catalyst	1292 $\pm$ 69 mW/m^2	Wastewater	ter Heijne et al. [44]
Carbon-based	Graphene oxide	Carbon paper	Ti	102 mW/m^2	*S. oneidensis MR-1*	Zhao et al. [105]

(continued)

Table 2 (continued)

Type of materials	Anode	Cathode	Catalyst	Power density	Inoculum source/bacteria	References
Carbon-based	3D-Graphene	Carbon cloth	Pt	1516 ± 87 mW/m^2	*E. coli*	Osgood et al. [100]
Carbon-based	Graphene	Carbon cloth	Pt	2850 mW/m^2	*E. coli*	Najafabadi et al. [123]
Carbon-based	rGO sheets/carbon cloth	carbon cloth	Pt	2.5 W/m^3	Anaerobic sludge	Xiao et al. [124]
Carbon-based	Carbon cloth/CNTs	Carbon cloth/CNTs	Pt	65mW/m^2	Domestic wastewater acetate	Tsai et al. [125]
Carbon-based	Graphene oxide with CNT	Carbon cloth	Pt	434 mWm^{-2}	*E. coli*	kumar et al. [126]
Carbon-based	Non-wet-proof carbon paper	Non-wet-proof carbon paper	Pt	188 mWm^{-2}	Mixed community	Hassan et al. [127]
Carbon-based	Carbon felt	Carbon fiber felt	Pt	784 mW/m^2	Anaerobic sludge	Yang et al. [128]
Carbon-based	Glassy carbon	Carbon cloth	Pt	1905 mW/m^2	Anaerobic sludge	Yuan et al. [129]
Carbon-based	Carbon brush	Carbon cloth with gas diffusion layers	Ti	4.25 mW/m^2	Sludge	Choi and Cui [130]
Carbon-based	Graphite brush	Carbon cloth	Pt	1280 mW/m^2	Native wastewater	Santoro et al. [131]
Carbon-based	Carbon paper	Carbon paper	Pt	600mW/m^2	Primary clarifier overflow	Wei et al. [8]
Carbon-based	Graphene coating on Carbon cloth	Carbon cloth	Pt	52.5 mW/m^2	*P. aeruginosa*	Liu et al. [132]
Carbon-based	Graphene oxide modification with carbon paper	Carbon paper	–	368 mW/m^2	Anaerobic Sludge	Guo et al. [133]
Carbon-based	Graphene nanosheet coating on carbon paper	Carbon cloth	Pt	610 mW/m^2	*S. oneidensis MR-1*	Ma et al. [107]

(continued)

Table 2 (continued)

Type of materials	Anode	Cathode	Catalyst	Power density	Inoculum source/bacteria	References
Composite-based	Polypyyrole/ graphene oxide	Carbon felt	Pt	1326 mWm^{-2}	S. oneidensis	Lv et al. [134]
Composite- based	TiO_2 and rGO composite	Carbon fiber/brush	Ti	3169 mW/m^2	*S. putrefaciens CN32*	Zou et al. [135]
Composite-based	Graphene/Au composite	Carbon paper	Pt	508 mW/m^2	*S. oneidensis MR-1*	Zhao et al. [136]
Composite-based	Graphite plates	Platinum meshes	–	1410 mW/m^2	*Shewanellaonei densi*	Dewan et al. [137]
Composite-based	Zero-dimension nitrogen doped carbon dots modification with carbon paper	Carbon paper	Pt	0.32 mW/m^2	*Pseudomonas*	Guan et a. [138]
Composite-based	Graphene/PPy	Carbon cloth	Without catalyst	145 mW/m^2	*S. oneidensis MR-1*	Yong et al. [139]
Composite-based	N-doped graphene nanosheets (NGNS) on carbon cloth	carbon cloth	Pt	1008 mW/m^2	*E. coli*	Kirubaharan et al. [140]
Composite-based	rGO/SnO_2/Carbon cloth	Pt rod	Pt	1624 mW/m^2	E. coli	Mehdinia et al. [141]
Metal and metal oxides	Stainless steel mesh coated with carbon cloth	Carbon black	Pt	1610 ± 56 mW/m^2	Domestic wastewater	Zhang et al. [142]
Metal and metal oxide	Ti/TiO_2	Pt meshes	Pt	2317 W/m^3	Swamp sediments	Benetton et al. [143]
Metal	Stainless steel	Stainless steel	Pt	23 mW/m^2	Marine sediments	Dumas et al. [144]
Metal and metal oxide	Titanium	–	Pt	–	*G. sulfurreducens*	Dominguez-Benetton et al. [145]

(continued)

Table 2 (continued)

Type of materials	Anode	Cathode	Catalyst	Power density	Inoculum source/bacteria	References
Metal and metal oxide	Titanium rod	graphite felt	Pt	–	Pre-acclimated bacteria	Michaelidou et al. [146]
Carbon-based polymer composite	RGO/carbon cloth-PANI	Carbon felt	Pt	1390 mWm^{-2}	Anaerobic Sludge	Hou et al. [147]
Carbon-based + polymer composite	rGO/PPy	Carbon paper	Pt	1068 mW/m^2	*E. coli*	Gnana Kumar et al. [88]
Carbon-based + polymer composite	Polypyyrole coating on carbon cloth	Granular activated carbon	Pt	5 W/m^3	Domestic wastewater	Jiang and Li [148]
Carbon-based + polymer composite	Nickel foam/CNTs/PANI	carbon cloth	Without catalyst	113 W/m^3	*Shewanella Sp*	Nourbakhsh et al. [149]
Carbon-based + polymer composite	Graphene powder/polytetrafluoroethylene on Carbon cloth	Carbon cloth	Pt	0.329 mW/m^2	Anaerobic pretreated sludge	Pareek et al. [150]
Carbon-based + polymer composite	Polyaniline (PANI) networks onto graphene nanoribbons (GNRs)-coated on carbon Paper (CP/GNRs/PANI)	Carbon paper	Ti	856 mW/m^2	*S. oneidensis MR-1*	Chen et al. [104]

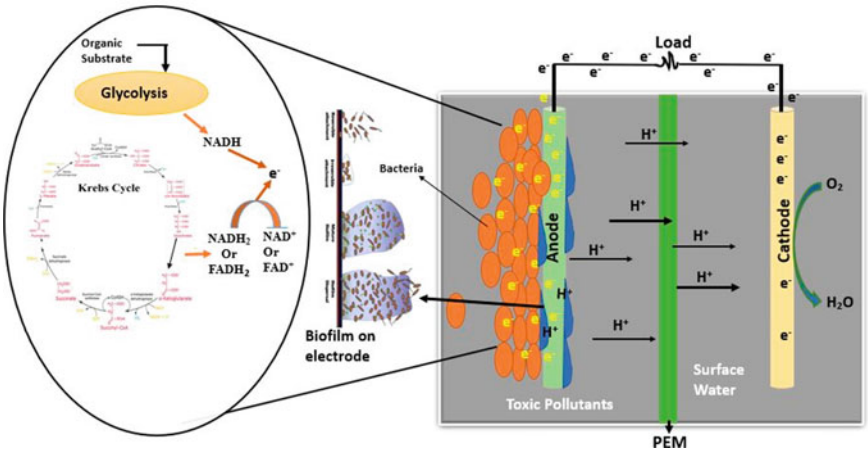

Fig. 2 Functioning of the electrode in MFCs. Adapted from reference [25] with MDPI permission

through MFC in presence of *Dysgonomonas and Klebsiella.* The power density of MFCs after seven days of operation with a 200 mg/L starting concentration of anaerobic sludge was 529 12 mW/m^2. Jiang et al. [156] looked at wastewater from the oil sands process to see if MFCs could create electricity while also treating oil sand tailings. The MFCs cleaned various heavy metals from wastewater derived from the oil sands process with constant energy production and with good outputs of efficiencies percentages. The removal efficiency was somehow low due to the usage of carbon derivatives as cathode and anode. For a variety of reasons, the carbon fiber felt outperformed the carbon cloth, but graded anode and surface region available to bacteria were essential. Habibul et al. [157] utilized a graphite manufactured anode to research electro kinetic biosorption of heavy metals from disturbed soils, in order to improve the anode's quality. However, research into the breakdown of particularly harmful metals such as cadmium, lead, and mercury is scarce. Bacteria require high-quality anode materials to digest harmful elements from the water supply. Similarly, the researchers utilized various MFC used anodic chamber agents to decolorize the organic dyes that were damaging the ecosystem. Fang et al. [158] investigated the potential of MFCs which are made of activated carbon and a cathode built of stainless-steel mesh to process azo dye. The decolorization rate was high due to articulated carbon serving as an anode. To decolorize methyl orange from anaerobic sludge, Kawale et al. [159] utilized a graphitic rod as an anode to decolorize methyl orange from anaerobic sludge. Both decolorization and energy output were significantly influenced by the electrode. However, several researchers used MFCs with various anode materials to remove organic contaminants. Kabutey et al. [160] utilized a macrophyte cathode silt microbial power module to research the evacuation of natural impurities and energy age from metropolitan waterway dregs. Carbon fiber was utilized as both cathode and anode terminals in this investigation, with an expulsion proficiency of 28.2%. Microorganisms like *Euryarchaeota and Proteobacteria*

were unable to separate phosphorus due to its acidic nature and inefficient ability of cathode used in this work. Marks et al. [161] investigated the functioning of MFCs in anoxic surroundings and found that they could remove 22% of nitrate from anaerobic sludge. The cathode and anode electrodes in this experiment were graphite plates. According to an exhaustive literature study, the authors determined that different types of anode materials are utilized under different situations since MFC functioning is influenced by a variety of parameters. One of the most significant functions of an anode is to give bacteria sufficient surface area for respiration while also assisting them in carrying electrons from colonization of bacterium to the cathode via an outer circuit. As a result, it has been shown that employing a high-graded anode will yield superior outcomes with less environmental constraints. Many difficulties that cause disruption during processing, such as long-term stability, might be addressed using this high-quality material. To reduce metal corrosion, we may fabricate anode more efficiently with the help of conductive material and high surface regions materials like composite materials, graphene, and its derivatives, containing metal/metal oxides. As a result, in order to get better outcomes for remediation purposes, the anode should be unique and efficient.

7 Influence of Electrode (Anode/Cathode) on Energy Production

MFCs as an innovative approach opened new avenues in the domain of ecosystem pollution and its safe elimination. MFCs generate energy from various organic waste materials using microorganisms as exoelectrogens [162, 163]. In Single chamber MFCs, 3D terminal materials and the improved anodes are utilized for the generation of energy. [128]. Many materials and operating parameters were regularly modified at the start, making it difficult to pinpoint the aspects that helped improve the present generation over traditional approaches. In view of the progression of this framework, more consideration is currently needed to produce a more prominent electrical yield [164, 165]. The electrode is straightforwardly connected to the creation of power. The production of energy rises as the electrode's strength and conductivity improve. Wang et al. [96] additionally demonstrated proficiency of carbon felt as an anode within sight of platinum in form of impetus, but force creation was exceptionally low. Zhang et al. [154] utilized the incorporated adsorption method to separate chromium from anaerobic assimilation ooze and had the option to accomplish a current force of 343 mV. Utilizing engineered arrangements, Liu et al. [166] explored MFC execution utilizing carbon fabric as both terminals within sight of Fe/Ni/actuated carbon as an impetus and delivered remarkable energy yield. To improve the material, Santoro et al. [131] utilized graphite brushes within sight of Pt impetus SMFCs to accomplish a high energy yield. In the wake of utilizing local wastewater as an inoculum source, a force thickness of 1280 mW/m^2 was reached. The performance of the electrodes determines the amount of energy produced. Carbon felt, for example, has a lower

surface area and conductive efficiency than graphite-based materials. As a result, graphite-based materials produce multiple times the results of carbon-derived items. Nguyen et al. [167] reported a novel method to develop a high quality anode's material. Zhang et al. [168] recently published a paper describing the outstanding electrochemical presentation of MFCs with an allotropic form of carbon named graphene oxide for electrode enhancing performance. When contrasted with other carbon-based materials, graphene oxide further developed electron transport and created more energy. Therefore, graphene is preferable and encouraging material for the fabrication of electrode (anode/cathode) in MFCs.

Natural assets, on the other hand, are used in current research for anode fabrication since they are practical and elite materials when contrasted with manufactured materials. Yang et al. [169] found that banana strips and underwater wetland dregs, which were utilized as an inoculum hotspot for MFC activity, straightforwardly created energy. Accordingly, utilizing regular materials as terminals (anodes/cathode) is a viable answer for tending to introduce difficulties and orchestrating excellent anode materials, like GO and derivatives modified with metal oxides. The attributes of the anode can be improved by joining GO composites with metal oxides. Anodes made of ZnO/GO, Fe_2O_3/GO, and CuO/GO are generally utilized in MFCs to acquire high power execution. From the last few decades, low-cost anode and cathode materials have been developed for the removal of toxic pollutants with energy generation in MFCs system (Table 3).

8 Challenges and Future Recommendations

Regardless of the multitude of advancements in MFCs, mainstream researchers actually face numerous difficulties and issues as far as power age and aqueous treatment. It must be evidently quick advancement in designing MFCs as productive and preferable. Besides, reactors of various plans have already been presented, such as one and two-fold chambers, film less, H-shape, and rounded MFCs [191, 192]. Basically, the primary objective of all improvements is to accomplish commonsense execution of MFCs for remediation purposes at a business level. The principal segment in MFCs is the anode, that additionally dependable somewhat for their financial and functional capability. There are a few challenges related to electrode (anode/cathode) that have reduced the use of MFCs on a modern level:

1. The electrode components are crucial for the monetary province of MFCs. Thusly, removing costs for materials is a significant issue for executions in MFC applications. To resolve this matter, we ought to consider the waste material sources and converted them into carbonized structures that can be furthermore used as terminal material in a couple of constructions, similar to posts, brushes, bars, and plates. Nevertheless, one more technique is the improvement of composites with metals and utilizing polymers to fabricate them more compelling at an insignificant cost [193].

Table 3 Influence of the electrode (anode/cathode) on removal efficiency and energy production through MFCs

Category of pollutant	suspected analytes	Anode	Cathode	Source	Removal efficiency %	Reference
	Cu^{2+}	Carbon brush	Reduced Graphene oxide	*Geobacter and Pseudomonas*	98	Abourached et al. [170]
	Cu^{2+}	Graphite felt	Graphite plate	Anaerobic sludge	70	Wang et al. [171]
	$CuSO_4$/CuO	Graphite plate	Graphite felt	Anaerobic sludge	>99	Tao et al. [172]
	Co	Graphite felt	Graphite felt	Lithium cobalt oxide Solution	62.5 ± 1.8	Yun-Hai et al. [173]
	Cr (VI)	Graphite felt	Graphite rod	*Shewanella oneidensis MR-1*	67	Singhvi [174]
Metal-based water pollutant	Cr (VI)	Graphite felts	Graphite felts	*Actinobacteria, B-Proteobacteria*	5 mg/L with 93 25 mg/L with 61	Tao et al. [175]
	Cr (VI)	Carbon fiber felt	Carbon fiber felt	Anaerobic sludge	75.4 ± 1.9	Zhang et al. [154]
	Cr (VI)	Activated charcoal	Activated charcoal	Algae biomass	98	Ryu et al. [176]
	Cr (VI)	Carbon felt	Carbon felt	*Shewanelladecolorationis S12, K. pneumonia*	99.9	Wu et al. [177]
	V(V)	Carbon fiber felt	Carbon fiber felt	*Dysgonomonas and Klebsiella*	60.7	Qiu et al. [155]
	V(V)	Carbon fiber felt	Carbon fiber felt	Anaerobic sludge	67.9 ± 3.1	Zhang et al. [154]
	Au^{3+}	Carbon brush	Carbon cloth	Tetrachloroaurate wastewater	99.89 ± 0.00	[178]
	Ag^{+} ions	Carbon brush	Carbon cloth	Sludge mixture	99.91	Zhang et al. [154]
	Ag^{+}	Carbon cloth	Graphite	NH_3 chelated silver waste water	99.9	Choi and Hu [179]

(continued)

Table 3 (continued)

Category of pollutant	suspected analytes	Anode	Cathode	Source	Removal efficiency %	Reference
	Platinum (Pt)	Graphite plate	Graphite plate	Anaerobic sludge bed	90	Li et al. [180]
	Zn	Carbon cloth (no wet proofing)	carbon cloth (30% wet proofing)	Sewage sludge	90	Huang et al. [181]
	Oil sands tailings	Carbon cloth	Carbon cloth with Pt coating	Oil sands tailings affected water	97.8 Se, 96.8 Ba, 77.1 Mo, 32.5 Pb	Jiang et al. [156]
	Active brilliant red X-3B	Porous carbon paper	Porous carbon paper	Aerobic sludges	90	Chen et al. [182]
	Methyl orange	Unpolished graphite	Rutile—coated graphite	Anaerobic sludge	73.4	[159]
	Acid navy blue R	Graphite rods	Graphite rods	Anaerobic sludge	–	Solanki et al. [183]
Dyes-based water pollutant	Congo RED	Graphite felt	Carbon paper	Anaerobic sludge	70	Li et al. [184]
	Acid Orange 7	Graphite rod	Graphite rod	Microbial consortium	78	Liu et al. [185]
	Azo dye	Carbon felt	Carbon felt	Mixed-culture sludge	94	Khan et al. [186]
	Model textile dyes	Activated carbon	Hydrophobic carbon cloth	*Proteus hauseri*	75	Ding et al. [187]
	Thionine-based textile dyes	Porous carbon cloth	Porous carbon cloth	*Proteus hauseri*	50	Li et al. [71]
	Amaranth	Granular graphite	Spectrographic pure graphite	–	82.59	Mu et al. [188]
	Congo red	Plain carbon papers (non-wet proofed)	Carbon paper (wetproofed)	Culture of aerobic and sludge	85	Sun et al. [189]
	Acid orange 7	Carbon cloth	Carbon cloth	*Shewanellaoneidensis*	>98	Sun et al. [190]

(continued)

Table 3 (continued)

Category of pollutant	suspected analytes	Anode	Cathode	Source	Removal efficiency %	Reference
	Azo dye	Activate carbon	Stainless steel mesh	Concentrated anaerobic sludge	96.5	Jiang et al. [156]

2. During the creation of an electrode, the cover is indispensable for assembling material in its ideal shape. To confirm the assurance of an astoundingly essential factor for researchers to develop materials to make it firmer and steadier. It is alluring to find more sensible and spending plan agreeable folios for the terminal (anode/cathodes).
3. The size and setup are imperative viewpoints in the creation of electrodes. The surface area of electrode play significant role in bacterial growth and electron transferred from negative to positive terminal in MFCs [194].
4. Adjustment of the electrode has made critical redesigns regards to power age and the bioremediation of wastewater. So that, material parts and fitting standards stay dim. Researchers ought to discover more authentic parts for preferable adjustments.
5. One flaw is the long-term steadiness of electrodes at the bulk level. At present, for the genaration of energy, nobody has yet explored the strength of electrode for long term use [195, 196]. Steadiness is a significant issue that resists MFCs functioning at a mechanical scale. Accordingly, scientists should carry on tracking a compelling manufacturing procedure for electrodes while remembering the strength factor for electrode materials. An exceptionally steady fastener like nafion or polysulfides can be utilized to tie the graphene derivatives to keep up with long-term steadiness.

9 Conclusion

The impacts of electrode (cathode/anode) in MFCs were summarized in this chapter. Carbon-graded materials, conductive polymers, composite-based materials, and metal/metal oxide-based materials have all been proposed as electrode materials in MFCs. The adhesion of bacteria and the growth of biofilm are major areas of progress in the development of electrodes. To achieve higher biofilm densities, significant effort has been put into expanding the surface area of electrode materials. As indicated in this chapter, there are a variety of different materials proposed for use as anodes or cathodes. Notwithstanding, there is as yet a critical hole in the advancement of conceivable cathode materials. A terminal (anode/cathode) in MFCs can be made of incredibly spongy and conductive materials like metallic composites and 3D graphene. During long haul MFCs activity, cathode materials should be amazingly steady in wastewater. These qualities make a terminal more significant on a modern scale when it stays stable for quite a while. A terminal material should thusly have a huge pore size to forestall issues in the bioremediation of wastewater applications from being discouraged. The utilization of MFCs is mainly depend on the material expense and surface modification of electrode. Cheap and accessible materials and effective methods should, therefore, be introduced in the MFCs applications industry for metallic or polymer nanocomposite or carbon-based electrons. In future, the testing of upscaling of resource anodes should be a key effort. It is vital to develop an electrode/diaphragm collection for excellent membrane assembly for

practical use. But the anode efficiency available is still not enough to be used on a business level. Further studies should focus on the use and optimization of waste material to fabricate electrodes.

Acknowledgments The authors would like to express their appreciation to the School of Chemical Sciences, USM.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Umar K, Yaqoob AA, Ibrahim MNM, Parveen T, Safian MT (2020) Environmental applications of smart polymer composites. Smart Polym Nanocompos Biomed Environ Appl 15:295–320
2. Ahmad A, Setapar SH, Yaqoob AA, Ibrahim MNM (2021) Synthesis and characterization of GO-Ag nanocomposite for removal of malachite dye from aqueous solution, Mater Today: Proc 12
3. Ibrahim N, Zainal SFFS, Aziz HA (2018) Application of UV-based advanced oxidation processes in water and wastewater treatment, 384–414. https://doi.org/10.4018/978-1-5225-5766-1.ch014
4. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337:686–690. https://doi.org/10.1126/science.1217412
5. Yaqoob AA, Khatoon A, Setapar SHM, Umar K, Parveen T, Ibrahim MNM, Ahmad A, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10:819
6. Asim AY, Ibrahim MNM, Khalid U, Tabassum P, Akil A, Lokhat D, Siti HA (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desal Water Treat 214:379–389
7. Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C (2021) Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov 21:101579
8. Wei J, Liang P, Huang X (2011) Recent progress in electrodes for microbial fuel cells. Bioresour Technol 102:9335–9344. https://doi.org/10.1016/j.biortech.2011.07.019
9. ElMekawy A, Hegab HM, Losic D, Saint CP, Pant D (2017) Applications of graphene in microbial fuel cells: the gap between promise and reality. Renew Sustain Energy Rev 72:1389–1403. https://doi.org/10.1016/j.rser.2016.10.044
10. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S (2020) Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview. BiochemEng J 3:107779
11. Cai T, Meng L, Chen G, Xi Y, Jiang N, Song J, Zheng S, Liu Y, Zhen G, Huang M (2020) Application of advanced anodes in microbial fuel cells for power generation: a review. Chemosphere 248. https://doi.org/10.1016/j.chemosphere.2020.125985
12. Logan BE, Wallack MJ, Kim KY, He W, Feng Y, Saikaly PE (2015) Assessment of microbial fuel cell configurations and power densities. Environ Sci Technol Lett 2:206–214. https://doi.org/10.1021/acs.estlett.5b00180
13. Yaqoob AA, Ibrahim MNM, Umar K, Bhawani SA, Khan A, Asiri AM, Khan MR, Azam M, AlAmmari AM (2021) Cellulose derived graphene/polyaniline nanocomposite anode for

energy generation and bioremediation of toxic metals via benthic microbial fuel cells. Polymer 13:135
14. Yaqoob AA, Ibrahim MNM, Umar K (2021) Electrode material as anode for improving the electrochemical performance of microbial fuel cells. In: Energy storage battery systems-fundamentals and applications. IntechOpen
15. Yaqoob AA, Serrà A, Ibrahim MNM, Yaakop AS (2021) Self-assembled oil palm biomass-derived modified graphene oxide anode: an efficient medium for energy transportation and bioremediating Cd (II) via microbial fuel cells. Arabian J Chem 14:103121
16. Kirubaharan CJ, Kumar GG, Sha C, Zhou D, Yang H, Nahm KS, Raj BS, Zhang Y, Yong YC (2019) Facile fabrication of Au@polyaniline core-shell nanocomposite as efficient anodic catalyst for microbial fuel cells. Electrochim Acta 328:135136. https://doi.org/10.1016/j.electacta.2019.135136
17. Mustakeem (2015) Electrode materials for microbial fuel cells: nanomaterial approach. Mater Renew Sustain Energy 4:1–11. https://doi.org/10.1007/s40243-015-0063-8
18. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S, Ahmad A (2021) Preparation, characterization, and application of modified carbonized lignin as an anode for sustainable microbial fuel cell. Pro Safe Environ Protect. 155:49–60
19. Schröder U, Patil SA, Di Lorenzo M, Gonzalez Olias L, Cameron PJ (2019) Effect of electrode properties on the performance of a photosynthetic microbial fuel cell for atrazine detection. Front Energy Res 7:105. Www.Frontiersin.Org. https://doi.org/10.3389/fenrg.2019.00105
20. Yaqoob AA, Ibrahim MNM, Umar K. Yaakop AS, Ahmad A (2021) Modified graphene oxide anode: a bioinspired waste material for bioremediation of Pb^{2+} with energy generation through microbial fuel cells. Chem Eng J 417:128052
21. Yaqoob AA, Ibrahim MNM, Umar K (2021) Biomass-derived composite anode electrode: synthesis, characterizations, and application in microbial fuel cells (MFCs). J Environ Chem Eng 9:106111
22. Kamedulski P, Ilnicka A, Lukaszewicz JP, Skorupska M (2019) Highly effective three-dimensional functionalization of graphite to graphene by wet chemical exfoliation methods. Adsorption 25:631–638. https://doi.org/10.1007/s10450-019-00067-9
23. Hindatu Y, Annuar MSM, Gumel AM (2017) Mini-review: Anode modification for improved performance of microbial fuel cell. Renew Sustain Energy Rev 73:236–248. https://doi.org/10.1016/j.rser.2017.01.138
24. Yaqoob AA, Umar K, Ibrahim MNM (2020) Silver nanoparticles: various methods of synthesis, size affecting factors and their potential applications—A review. Appl Nanosci 10:1369–1378. https://doi.org/10.1007/s13204-020-01318-w
25. Yaqoob AA, Nasir M, Ibrahim M, Rafatullah M, Shen Chua Y, Ahmad A, Umar K (n.d.) Materials recent advances in anodes for microbial fuel cells: an overview. https://doi.org/10.3390/ma13092078
26. Senthilkumar N, Pannipara M, Al-Sehemi AG, Gnana kumar G (2019) PEDOT/$NiFe_2O_4$ nanocomposites on biochar as a free-standing anode for high-performance and durable microbial fuel cells. New J Chem 43:7743–7750. https://doi.org/10.1039/C9NJ00638A
27. Sauerteig D, Hanselmann N, Arzberger A, Reinshagen H, Ivanov S, Bund A (2018) Electrochemical-mechanical coupled modeling and parameterization of swelling and ionic transport in lithium-ion batteries. J Power Sour 378:235–247. https://doi.org/10.1016/j.jpowsour.2017.12.044
28. Kang YL, Pichiah S, Ibrahim S (2017) Facile reconstruction of microbial fuel cell (MFC) anode with enhanced exoelectrogens selection for intensified electricity generation. Int J Hydrog Energy 42:1661–1671. https://doi.org/10.1016/j.ijhydene.2016.09.059
29. Islam AKMS, Hussain RT, Khairuddean M, MohdSuah FB, Ahmed NM (2021) Innovative approaches to synthesize novel graphene materials. Curr Nanosci 17. https://doi.org/10.2174/1573413717666210208183349
30. Li B, Zhou J, Zhou X, Wang X, Li B, Santoro C, Grattieri M, Babanova S, Artyushkova K, Atanassov P, Schuler AJ (2014) Surface modification of microbial fuel cells anodes: approaches to practical design. Electrochim Acta 134:116–126. https://doi.org/10.1016/j.electacta.2014.04.136

31. Fadzli FS, Rashid M, Yaqoob AA, Ibrahim MNM (2021) Electricity generation and heavy metal remediation by utilizing yam (Dioscorea alata) waste in benthic microbial fuel cells (BMFCs). Biochem Eng J 172:108067
32. Srivastava P, Yadav AK, Mishra BK (2015) The effects of microbial fuel cell integration into constructed wetland on the performance of constructed wetland. Bioresour Technol 195:223–230. https://doi.org/10.1016/j.biortech.2015.05.072
33. Wang K, Liu Y, Chen S (2011) Improved microbial electrocatalysis with neutral red immobilized electrode. J Power Sour 196:164–168. https://doi.org/10.1016/j.jpowsour.2010.06.056
34. Borsje C, Liu D, Sleutels THJA, Buisman CJN, ter Heijne A (2016) Performance of single carbon granules as perspective for larger scale capacitive bioanodes. J Power Sour 325:690–696. https://doi.org/10.1016/j.jpowsour.2016.06.092
35. Yaqoob AA, Ibrahim MNM, Yaakop AS, Ahmad A (2021) Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. App Nanosci 11:1949–1961
36. Sonawane JM, Yadav A, Ghosh PC, Adeloju SB (2017) Recent advances in the development and utilization of modern anode materials for high performance microbial fuel cells. Biosens Bioelectron 90:558–576. https://doi.org/10.1016/j.bios.2016.10.014
37. Sokol NW, Bradford MA (2019) Microbial formation of stable soil carbon is more efficient from belowground than aboveground input. Nat Geosci 12:46–53. https://doi.org/10.1038/S41561-018-0258-6
38. Li F, Sharma Y, Lei Y, Li B, Zhou Q, Li F, Zhou Q, Sharma Y, Li B, Lei Y (2010) Microbial fuel cells: the effects of configurations, electrolyte solutions, and electrode materials on power generation. Appl Biochem Biotechnol 160:168–181. https://doi.org/10.1007/s12010-008-8516-5
39. Zhao F, Rahunen N, Varcoe JR, Chandra A, Avignone-Rossa C, Thumser AE, Slade RCT (2008) Activated carbon cloth as anode for sulfate removal in a microbial fuel cell. Environ Sci Technol 42:4971–4976. https://doi.org/10.1021/es8003766
40. Wang X-D, Xu Y-F, Rao H-S, Xu W-J, Chen H-Y, Zhang W-X, Kuang D-B, Su C-Y (2016) Novel porous molybdenum tungsten phosphide hybrid nanosheets on carbon cloth for efficient hydrogen evolution. Energy Environ Sci 9:1468–1475. https://doi.org/10.1039/C5EE03801D
41. Yaqoob AA, Ibrahim MNM, Ahmad A, Khatoon A, Setapar SH (2021) Polyaniline-based materials for supercapacitors. Handbook of supercapacitor materials: synthesis, characterization, and applications 1:113–130
42. Bhamare YM, Koinkar P, Furube A, More MA (2019) Femtosecond transient absorption spectroscopy of laser-ablated graphite and reduced graphene oxide for optical switching behavior. Opt Mater X 2:100026. https://doi.org/10.1016/j.omx.2019.100026
43. Ren Z, Meng N, Shehzad K, Xu Y, Qu S, Yu B, Luo J (2015) Mechanical properties of nickel-graphene composites synthesized by electrochemical deposition. Nanotechnology 26(6):65706
44. ter Heijne A, Hamelers HVM, Saakes M, Buisman CJN (2008) Performance of non-porous graphite and titanium-based anodes in microbial fuel cells. Electrochim Acta 53:5697–5703. https://doi.org/10.1016/j.electacta.2008.03.032
45. Lowy DA, Tender LM, Zeikus JG, Park DH, Lovley DR (2006) Harvesting energy from the marine sediment-water interface II. Kinetic activity of anode materials. BiosensBioelectron 21: 2058–2063. https://doi.org/10.1016/j.bios.2006.01.033
46. Yazdi AA, D'Angelo L, Omer N, Windiasti G, Lu X, Xu J (2016) Carbon nanotube modification of microbial fuel cell electrodes. Biosens Bioelectron 85:536–552. https://doi.org/10.1016/j.bios.2016.05.033
47. Zhang C, Liang P, Yang X, Jiang Y, Bian Y, Chen C, Zhang X, Huang X (2016) Binder-free graphene and manganese oxide coated carbon felt anode for high-performance microbial fuel cell. Biosens Bioelectron 81:32–38. https://doi.org/10.1016/j.bios.2016.02.051
48. Sun H, Xu S, Zhuang G, Zhuang X (2016) Performance and recent improvement in microbial fuel cells for simultaneous carbon and nitrogen removal: a review. J Environ Sci (China) 39:242–248. https://doi.org/10.1016/j.jes.2015.12.006

49. Sonu K (2017) Generation of bio-electricity from sewage sludge using single chamber microbial fuel cell. J Environ Sci Public Heal 01:68–74. https://doi.org/10.26502/jesph.96120007
50. Guo X, Zhan Y, Chen C, Cai B, Wang Y, Guo S (2016) Influence of packing material characteristics on the performance of microbial fuel cells using petroleum refinery wastewater as fuel. Renew Energy 87:437–444. https://doi.org/10.1016/j.renene.2015.10.041
51. Yasri NG, Nakhla G (2016) Electrochemical behavior of anode-respiring bacteria on doped carbon electrodes. ACS Appl Mater Interfaces 8:35150–35162. https://doi.org/10.1021/acsami.6b09907
52. Bhanvase BA, Shende TP, Sonawane SH (2016) Environmental technology reviews a review on graphene-TiO_2 and doped graphene-TiO_2 nanocomposite photocatalyst for water and wastewater treatment) a review on graphene-TiO_2 and doped graphene-TiO_2 nanocomposite photocatalyst for water and wastewater treatment. Environ Technol Rev 6:1–14. https://doi.org/10.1080/21622515.2016.1264489
53. Agnoli S, Favaro M (2016) Doping graphene with boron: a review of synthesis methods, physicochemical characterization, and emerging applications. J Mater Chem A 4:5002–5025. https://doi.org/10.1039/C5TA10599D
54. Tan RKL, Reeves SP, Hashemi N, Thomas DG, Kavak E, Montazami R, Hashemi NN (2017) Graphene as a flexible electrode: review of fabrication approaches. J Mater Chem A 5:17777–17803. https://doi.org/10.1039/C7TA05759H
55. Deng Y, Fang C, Chen G (2016) The developments of SnO_2/graphene nanocomposites as anode materials for high performance lithium ion batteries: a review. J Power Sour 304:81–101. https://doi.org/10.1016/j.jpowsour.2015.11.017
56. Gao Y (2012) Graphene and polymer composites for supercapacitor applications: a review. https://doi.org/10.1186/s11671-017-2150-5
57. Zhou G, Li L, Ma C, Wang S, Shi Y, Koratkar N, Ren W, Li F, Cheng HM (2015) A graphene foam electrode with high sulfur loading for flexible and high energy Li-S batteries. Nano Energy 11:356–365. https://doi.org/10.1016/j.nanoen.2014.11.025
58. Li F, Chen L, Knowles GP, Macfarlane DR, Zhang J (n.d.) Electrocatalysis hierarchical mesoporous SnO_2 nanosheets on carbon cloth: a robust and flexible electrocatalyst for CO_2 reduction with high efficiency and selectivity. https://doi.org/10.1002/ange.201608279
59. Hussain RT, Islam AKMS, Khairuddean M, Suah FBM (2021) A polypyrrole/GO/ZnO nanocomposite modified pencil graphite electrode for the determination of andrographolide in aqueous samples. Alex Eng J. https://doi.org/10.1016/j.aej.2021.09.040
60. Slate AJ, Whitehead KA, Brownson DAC, Banks CE (2019) Microbial fuel cells: an overview of current technology. Renew Sustain Energy Rev 101:60–81. https://doi.org/10.1016/j.rser.2018.09.044
61. Kanwal A, Yaqoob AA, Siddique A, Bhawani SA, Ibrahim MNM, Umar K (2021) Hybrid nanocomposites based on graphene and its derivatives: from preparation to applications. In: Graphene and nanoparticles hybrid nanocomposites: from preparation to applications, p 261
62. Cheng Y, Mallavarapu M, Naidu R, Chen Z (2018) In situ fabrication of green reduced graphene-based biocompatible anode for efficient energy recycle. Chemosphere 193:618–624. https://doi.org/10.1016/j.chemosphere.2017.11.057
63. Singh S, Bairagi P, Verma N (2018) Candle soot-derived carbon nanoparticles: an inexpensive and efficient electrode for microbial fuel cells. Electrochim Acta 264:119–127. https://doi.org/10.1016/j.electacta.2018.01.110
64. Bose D, Sridharan S, Dhawan H, Vijay P, Gopinath M (2019) Biomass derived activated carbon cathode performance for sustainable power generation from microbial fuel cells. Fuel 236:325–337. https://doi.org/10.1016/j.fuel.2018.09.002
65. Hung Y-H, Liu T-Y, Chen H-Y (2019) Renewable coffee waste-derived porous carbons as anode materials for high-performance sustainable microbial fuel cells. ACS Sustain Chem Eng 7:16991–16999. https://doi.org/10.1021/acssuschemeng.9b02405
66. Chang WT, Chao YH, Li CW, Lin KL, Wang JJ, Kumar SR, Lue SJ (2019) Graphene oxide synthesis using microwave-assisted versus modified Hummer's methods: efficient fillers for

improved ionic conductivity and suppressed methanol permeability in alkaline methanol fuel cell electrolytes. J Power Sour 414:86–95. https://doi.org/10.1016/j.jpowsour.2018.12.020
67. Tang J, Yuan Y, Liu T, Zhou S (2015) High-capacity carbon-coated titanium dioxide core-shell nanoparticles modified three dimensional anodes for improved energy output in microbial fuel cells. J Power Sour 274:170–176. https://doi.org/10.1016/j.jpowsour.2014.10.035
68. Chen S, Tang J, Jing X, Liu Y, Yuan Y, Zhou S (2016) A hierarchically structured urchin-like anode derived from chestnut shells for microbial energy harvesting. Electrochim Acta 212:883–889. https://doi.org/10.1016/j.electacta.2016.07.077
69. Yuan Y, Liu T, Fu P, Tang J, Zhou S (2015) Conversion of sewage sludge into high-performance bifunctional electrode materials for microbial energy harvesting. J Mater Chem A 3:8475–8482. https://doi.org/10.1039/C5TA00458F
70. Li D, Deng L, Yuan H, Dong G, Chen J, Zhang X, Chen Y, Yuan Y (2018) N, P-doped mesoporous carbon from onion as trifunctional metal-free electrode modifier for enhanced power performance and capacitive manner of microbial fuel cells. Electrochim Acta 262:297–305. https://doi.org/10.1016/j.electacta.2017.12.164
71. Li F, Chen L, Knowles GP, MacFarlane DR, Zhang J (2017) Hierarchical mesoporous SnO_2 nanosheets on carbon cloth: a robust and flexible electrocatalyst for CO_2 reduction with high efficiency and selectivity. Angew Chem Int Ed 56:505–509. https://doi.org/10.1002/anie.201608279
72. Tang J, Chen S, Yuan Y, Cai X, Zhou S (n.d.) In situ formation of graphene layers on graphite surfaces for efficient anodes of microbial fuel cells. https://doi.org/10.1016/j.bios.2015.04.074
73. Huggins T, Wang H, Kearns J, Jenkins P, Ren ZJ (2014) Biochar as a sustainable electrode material for electricity production in microbial fuel cells. Bioresour Technol 157:114–119. https://doi.org/10.1016/j.biortech.2014.01.058
74. Zhang J, Li J, Ye D, Zhu X, Liao Q, Zhang B (2014) Tubular bamboo charcoal for anode in microbial fuel cells. J Power Sour 272:277–282. https://doi.org/10.1016/j.jpowsour.2014.08.115
75. Chen S, He G, Hu X, Xie M, Wang S, Zeng D, Hou H, Schröder U (2012) A three-dimensionally ordered macroporous carbon derived from a natural resource as anode for microbial bioelectrochemical systems. Chemsuschem 5:1059–1063. https://doi.org/10.1002/cssc.201100783
76. Yaqoob AA, Parveen T, Umar K, Nasir M, Ibrahim M (n.d.) Role of nanomaterials in the treatment of wastewater: a review. https://doi.org/10.3390/w12020495
77. Nitisoravut R, Thanh CND, Regmi R (2017) Microbial fuel cells: advances in electrode modifications for improvement of system performance microbial fuel cells: advances in electrode modifications for improvement of system performance. Int J Green Energy. https://doi.org/10.1080/15435075.2017.1326049
78. Erable B, Byrne N, Etcheverry L, Achouak W, Bergel A (2017) Single medium microbial fuel cell: stainless steel and graphite electrode materials select bacterial communities resulting in opposite electrocatalytic activities. Int J Hydrog Energy 42:26059–26067. https://doi.org/10.1016/j.ijhydene.2017.08.178
79. Santoro C, Arbizzani C, Erable B, Ieropoulos I (2017) Microbial fuel cells: from fundamentals to applications. A review. J Power Sour 356:225–244. https://doi.org/10.1016/j.jpowsour.2017.03.109
80. Torabiyan A, Nabi Bidhendi GR, Mehrdadi N, Javadi K (2014) Application of nano-electrode platinum (Pt) and nano-wire titanium (Ti) for increasing electrical energy generation in microbial fuel cells of synthetic wastewater with carbon source (Acetate). Int J Environ Res 8:453–460
81. Stariha S, Artyushkova K, Serov A, Atanassov P (2015) Non-PGM membrane electrode assemblies: optimization for performance. Int J Hydrog Energy 40:14676–14682. https://doi.org/10.1016/j.ijhydene.2015.05.185
82. Füeg M, Borjas Z, Estevez-Canales M, Esteve-Núñez A, Pobelov IV, Broekmann P, Kuzume A (2019) Interfacial electron transfer between Geobacter sulfurreducens and gold electrodes via carboxylate-alkanethiol linkers: effects of the linker length. Bioelectrochemistry 126:130–136. https://doi.org/10.1016/j.bioelechem.2018.11.013

83. Kaur G, Adhikari R, Cass P, Bown M, Gunatillake P (2015) Electrically conductive polymers and composites for biomedical applications. https://doi.org/10.1039/c5ra01851j
84. Shi Y, Ma C, Peng L, Yu G, Shi Y, Ma C, Peng L, Yu G (2015) Conductive "Smart" hybrid hydrogels with PNIPAM and nanostructured conductive polymers. https://doi.org/10.1002/adfm.201404247
85. Yaqoob AA, Umar K, Adnan R, Ibrahim MNM, Rashid M (2021) Graphene oxide–ZnO nanocomposite: an efficient visible light photocatalyst for degradation of rhodamine B. App Nanosci 11:1291–1302
86. Shahadat M, Bushra R, Khan MR, Rafatullah M, Teng TT (2014) A comparative study for the characterization of polyaniline based nanocomposites and membrane properties. RSC Adv 4:20686–20692. https://doi.org/10.1039/C4RA01040J
87. Phoon BL, Lai CW, Juan JC, Show P-L, Chen W-H (2019) A review of synthesis and morphology of $SrTiO_3$ for energy and other applications. Int J Energy Res 43:5151–5174. https://doi.org/10.1002/er.4505
88. Gnana kumar G, Kirubaharan CJ, Udhayakumar S, Ramachandran K, Karthikeyan C, Renganathan R, Nahm KS (2014) Synthesis, structural, and morphological characterizations of reduced graphene oxide-supported polypyrrole anode catalysts for improved microbial fuel cell performances. ACS Sustain Chem Eng 2:2283–2290. https://doi.org/10.1021/sc500244f
89. Dumitru A, Vulpe S, Radu A, Antohe S (2018) Influence of nitrogen environment on the performance of conducting polymers/CNTs nanocomposites modified anodes for microbial fuel cells (MFCs). Rom J Phys 63:10–15
90. Ates M, Eker AA, Eker B (2017) Carbon nanotube-based nanocomposites and their applications. J Adhes Sci Technol 31:1977–1997. https://doi.org/10.1080/01694243.2017.1295625
91. Larouche F, Tedjar F, Amouzegar K, Houlachi G, Bouchard P, Demopoulos GP, Zaghib K (2020) Progress and status of hydrometallurgical and direct recycling of Li-Ion batteries and beyond. Materials (Basel) 13. https://doi.org/10.3390/ma13030801
92. Li Z, Gong L (n.d.) Materials review research progress on applications of polyaniline (PANI) for electrochemical energy storage and conversion. https://doi.org/10.3390/ma13030548
93. Chen Y-M, Wang C-T, Yang Y-C, Chen W-J (2013) Application of aluminum-alloy mesh composite carbon cloth for the design of anode/cathode electrodes in Escherichia coli microbial fuel cell. Int J Hydrog Energy 38:11131–11137. https://doi.org/10.1016/j.ijhydene.2013.01.010
94. Yaqoob AA, Ibrahim MNM, Ahmad A, Reddy AVB (2020) Toxicology and environmental application of carbon nanocomposite. In: Environmental remediation through carbon based nanocomposites. Green Energy and Technology; Springer, Singapore
95. Chen S, Patil SA, Brown RK, Schröder U (2019) Strategies for optimizing the power output of microbial fuel cells: transitioning from fundamental studies to practical implementation. Appl Energy 233–234:15–28. https://doi.org/10.1016/j.apenergy.2018.10.015
96. Shi J-L, Qi R, Zhang X-D, Wang P-F, Fu W-G, Yin Y-X, Xu J, Wan L-J, Guo Y-G (2017) High-thermal- and air-stability cathode material with concentration-gradient buffer for Li-Ion batteries. ACS Appl Mater Interfaces 9:42829–42835. https://doi.org/10.1021/acsami.7b14684
97. Deng Q, Li X, Zuo J, Ling A, Logan B (2010) Power generation using an activated carbon fiber cathode in an upflow microbial fuel cell. J Power Sour 195:1130–1135. https://doi.org/10.1016/j.jpowsour.2009.08.092
98. Yaqoob AA, Noor M, Serrà A, Ibrahim MNM (2020) Advances and challenges in developing efficient graphene oxide-based ZnO photocatalysts for dye photo-oxidation. Nanomaterial 10:932
99. Ghasemi M, Ismail M, Kamarudin SK, Saeedfar K, Daud WRW, Hassan SHA, Heng LY, Alam J, Oh SE (2013) Carbon nanotube as an alternative cathode support and catalyst for microbial fuel cells. Appl Energy 102:1050–1056. https://doi.org/10.1016/j.apenergy.2012.06.003

100. Osgood H, Devaguptapu SV, Xu H, Cho J, Wu G (2016) Transition metal (Fe Co, Ni, and Mn) oxides for oxygen reduction and evolution bifunctional catalysts in alkaline media. Nano Today 11:601–625. https://doi.org/10.1016/j.nantod.2016.09.001
101. Huang L, Li X, Ren Y, Wang X (n.d.) A monolithic three-dimensional macroporous graphene anode with low cost for high performance of microbial fuel cell
102. Akbari E, Buntat Z (2017) Benefits of using carbon nanotubes in fuel cells: a review. Int J Energy Res 41:92–102. https://doi.org/10.1002/er.3600
103. Zhao C, Gai P, Liu C, Wang X, Xu H, Zhang J, Zhu J-J (2013) Polyaniline networks grown on graphene nanoribbons-coated carbon paper with a synergistic effect for high-performance microbial fuel cells. J Mater Chem A 1:12587–12594. https://doi.org/10.1039/C3TA12947K
104. Chen J, Deng F, Hu Y, Sun J, Yang Y (2015) Antibacterial activity of graphene-modified anode on Shewanella oneidensis MR-1 biofilm in microbial fuel cell. J Power Sour 290:80–86
105. Zhao C, Wang Y, Shi F, Zhang J, Zhu JJ (2013) High biocurrent generation in shewanella-inoculated microbial fuel cells using ionic liquid functionalized graphene nanosheets as an anode. Chem Commun 49:6668–6670. https://doi.org/10.1039/c3cc42068j
106. Iigatani R, Ito T, Watanabe F, Nagamine M, Suzuki Y, Inoue K (2019) Electricity generation from sweet potato-shochu waste using microbial fuel cells. J Biosci Bioeng 128:56–63. https://doi.org/10.1016/j.jbiosc.2018.12.015
107. Ma M, You S, Gong X, Dai Y, Zou J, Fu H (2015) Silver/iron oxide/graphitic carbon composites as bacteriostatic catalysts for enhancing oxygen reduction in microbial fuel cells. J Power Sour 283:74–83. https://doi.org/10.1016/j.jpowsour.2015.02.100
108. Zhang F, Cheng S, Pant D, Van Bogaert G, Logan BE (2009) Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. Electrochem Commun 11:2177–2179. https://doi.org/10.1016/j.elecom.2009.09.024
109. Zhao L, Deng J, Hou H, Li J, Yang Y (n.d.) Investigation of PAH and oil degradation along with electricity generation in soil using an enhanced plant-microbial fuel cell. J Clean Prod 221
110. Wang Y, Chen Y, Wen Q (2018) Microbial fuel cells: enhancement with a polyaniline/carbon felt capacitive bioanode and reduction of Cr(VI) using the intermittent operation. Environ Chem Lett 16:319–326. https://doi.org/10.1007/s10311-017-0678-3
111. Antolini E (2018) Photo-assisted methanol oxidation on Pt-TiO_2 catalysts for direct methanol fuel cells: a short review. Appl Catal B Environ 237:491–503. https://doi.org/10.1016/j.apcatb.2018.06.029
112. Mitov M, Chorbadzhiyska E, Rashkov R, Hubenova Y (2012) Novel nanostructured electrocatalysts for hydrogen evolution reaction in neutral and weak acidic solutions. Int J Hydrog Energy 37:16522–16526. https://doi.org/10.1016/j.ijhydene.2012.02.102
113. Behera M, Jana PS, Ghangrekar MM (2010) Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode. Bioresour Technol 101:1183–1189. https://doi.org/10.1016/j.biortech.2009.07.089
114. Daud NN, Ahmad A, Yaqoob AA, Ibrahim MNM (2021) Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. Environ Sci Pollut Res 28:62816–62827
115. Hou B, Lu J, Wang H, Li Y, Liu P, Liu Y, Chen J (2019) Performance of microbial fuel cells based on the operational parameters of biocathode during simultaneous Congo red decolorization and electricity generation. Bioelectrochemistry 128:291–297. https://doi.org/10.1016/j.bioelechem.2019.04.019
116. Wang X, Cheng S, Feng Y, Merrill MD, Saito T, Logan BE (2009) Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells. Environ Sci Technol 43:6870–6874. https://doi.org/10.1021/es900997w
117. Cheng S, Liu H, Logan BE (2006) Increased performance of single-chamber microbial fuel cells using an improved cathode structure. ElectrochemCommun 8:489–494. https://doi.org/10.1016/j.elecom.2006.01.010
118. Logan BE, Murano C, Scott K, Gray ND, Head IM (2005) Electricity generation from cysteine in a microbial fuel cell. Water Res 39:942–952. https://doi.org/10.1016/j.watres.2004.11.019

119. Clauwaert P, Rabaey K, Aelterman P, De Schamphelaire L, Pham TH, Boeckx P, Boon N, Verstraete W (2007) Biological denitrification in microbial fuel cells. Environ Sci Technol 41:3354–3360. https://doi.org/10.1021/es062580r
120. Clauwaert P, Van der Ha D, Boon N, Verbeken K, Verhaege M, Rabaey K, Verstraete W (2007) Open air biocathode enables effective electricity generation with microbial fuel cells. Environ Sci Technol 41:7564–7569. https://doi.org/10.1021/es0709831
121. You S-J, Ren N-Q, Zhao Q-L, Wang J-Y, Yang F-L (2009) Power generation and electrochemical analysis of biocathode microbial fuel cell using graphite fibre brush as cathode material. https://doi.org/10.1002/fuce.200900023
122. Qiao Y, Wen G-Y, Wu X-S, Zou L (2015) l-Cysteine tailored porous graphene aerogel for enhanced power generation in microbial fuel cells. RSC Adv 5:58921–58927. https://doi.org/10.1039/C5RA09170E
123. Najafabadi AT, Ng N, Gyenge E (2016) Electrochemically exfoliated graphene anodes with enhanced biocurrent production in single-chamber air-breathing microbial fuel cells. Biosens Bioelectron 81:103–110. https://doi.org/10.1016/j.bios.2016.02.054
124. Xiao L, Damien J, Luo J, Jang HD, Huang J, He Z (2012) Crumpled graphene particles for microbial fuel cell electrodes. J Power Sour 208:187–192. https://doi.org/10.1016/j.jpowsour.2012.02.036
125. Tsai H-Y, Wu C-C, Lee C-Y, Shih EP (2009) Microbial fuel cell performance of multiwall carbon nanotubes on carbon cloth as electrodes. J Power Sour 194:199–205. https://doi.org/10.1016/j.jpowsour.2009.05.018
126. Kumar GG, Hashmi S, Karthikeyan C, GhavamiNejad A, Vatankhah-Varnoosfaderani M, Stadler FJ (2014) Graphene oxide/carbon nanotube composite hydrogels—Versatile materials for microbial fuel cell applications. Macromol Rapid Commun 35:1861–1865. https://doi.org/10.1002/marc.201400332
127. Hassan SHA, Kim YS, Oh SE (2012) Power generation from cellulose using mixed and pure cultures of cellulose-degrading bacteria in a microbial fuel cell. Enzyme Microb Technol 51:269–273. https://doi.org/10.1016/j.enzmictec.2012.07.008
128. Yang W, Kim K-Y, Saikaly PE, Logan BE (2017) The impact of new cathode materials relative to baseline performance of microbial fuel cells all with the same architecture and solution chemistry. Energy Environ Sci 10:1025–1033. https://doi.org/10.1039/C7EE00910K
129. Yuan Y, Zhou S, Zhao B, Zhuang L, Wang Y (2012) Microbially-reduced graphene scaffolds to facilitate extracellular electron transfer in microbial fuel cells. Bioresour Technol 116:453–458. https://doi.org/10.1016/j.biortech.2012.03.118
130. Choi C, Cui Y (2012) Recovery of silver from wastewater coupled with power generation using a microbial fuel cell. Bioresour Technol 107:522–525. https://doi.org/10.1016/j.biortech.2011.12.058
131. Santoro C, Gokhale R, Mecheri B, Licoccia S, Serov A, Rtyushkova K, Atanassov A (n.d.) Design of Iron(II) phthalocyanine-derived oxygen reduction electrocatalysts for high-power-density microbial fuel cells. www.chemsuschem.org
132. Liu J, Qiao Y, Guo CX, Lim S, Song H, Li CM (2012) Graphene/carbon cloth anode for high-performance mediatorless microbial fuel cells. Bioresour Technol 114:275–280. https://doi.org/10.1016/j.biortech.2012.02.116
133. Guo W, Cui Y, Song H, Sun J (2014) Layer-by-layer construction of graphene-based microbial fuel cell for improved power generation and methyl orange removal. Bioprocess Biosyst Eng 37:1749–1758. https://doi.org/10.1007/s00449-014-1148-y
134. Lv Z, Chen Y, Wei H, Li F, Hu Y, Wei C, Feng C (2013) One-step electrosynthesis of polypyrrole/graphene oxide composites for microbial fuel cell application. Electrochim Acta 111:366–373. https://doi.org/10.1016/j.electacta.2013.08.022
135. Zou L, Qiao Y, Wu XS, Ma CX, Li X, Li CM (2015) Synergistic effect of titanium dioxide nanocrystal/reduced graphene oxide hybrid on enhancement of microbial electrocatalysis. J Power Sour 276:208–214. https://doi.org/10.1016/j.jpowsour.2014.11.127
136. Zhao C, Gai P, Song R, Zhang J, Zhu J-J (2015) Graphene/Au composites as an anode modifier for improving electricity generation in Shewanella-inoculated microbial fuel cells. Anal Methods 7:4640–4644. https://doi.org/10.1039/C5AY00976F

137. Dewan A, Beyenal H, Lewandowski Z (2008) Scaling up microbial fuel cells. Environ Sci Technol 42:7643–7648. https://doi.org/10.1021/es800775d
138. Guan YF, Zhang F, Huang BC, Yu HQ (2019) Enhancing electricity generation of microbial fuel cell for wastewater treatment using nitrogen-doped carbon dots-supported carbon paper anode. J Clean Prod 229:412–419. https://doi.org/10.1016/j.jclepro.2019.05.040
139. Yong Y-C, Dong X-C, Chan-Park MB, Song H, Chen P (2012) Macroporous and monolithic anode based on polyaniline hybridized three-dimensional graphene for high-performance microbial fuel cells. ACS Nano 6:2394–2400. https://doi.org/10.1021/nn204656d
140. Kirubaharan CJ, Santhakumar K, Kumar GG, Senthilkumar N, Jang J-H (2015) Nitrogen doped graphene sheets as metal free anode catalysts for the high performance microbial fuel cells. Int J Hydrog Energy 40:13061–13070
141. Mehdinia A, Ziaei E, Jabbari A (2014) Facile microwave-assisted synthesized reduced graphene oxide/tin oxide nanocomposite and using as anode material of microbial fuel cell to improve power generation. Int J Hydrog Energy 39:10724–10730. https://doi.org/10.1016/j.ijhydene.2014.05.008
142. Zhang B-G, Zhou S-G, Zhao H-Z, Shi C-H, Kong L-C, Sun J-J, Yang Y, Ni J-R (2010) Factors affecting the performance of microbial fuel cells for sulfide and vanadium (V) treatment. Bioprocess Biosyst Eng 33:187–194. https://doi.org/10.1007/s00449-009-0312-2
143. Benetton XD, Navarro-Ávila SG, Carrera-Figueiras C (2010) Electrochemical evaluation of Ti/TiO_2-polyaniline anodes for microbial fuel cells using hypersaline microbial consortia for synthetic-wastewater treatment. J New Mater Electrochem Syst 13:1–6. https://doi.org/10.14447/jnmes.v13i1.184
144. Dumas C, Mollica A, Féron D, Basséguy R, Etcheverry L, Bergel A (2007) Marine microbial fuel cell: use of stainless steel electrodes as anode and cathode materials. Electrochim Acta 53:468–473. https://doi.org/10.1016/j.electacta.2007.06.069
145. Dominguez-Benetton X, Srikanth S, Satyawali Y, Vanbroekhoven K, Pant D (2013) Enzymatic electrosynthesis: an overview on the progress in enzyme-electrodes for the production of electricity, fuels and chemicals. J MicrobBiochem Technol 5. https://doi.org/10.4172/1948-5948.s6-007
146. Michaelidou U, Ter Heijne A, Euverink GJW, Hamelers HVM, Stams AJM, Geelhoed JS (2011) Microbial communities and electrochemical performance of titanium-based anodic electrodes in a microbial fuel cell. Appl Environ Microbiol 77:1069–1075. https://doi.org/10.1128/AEM.02912-09
147. Hou J, Liu Z, Zhang P (2013) A new method for fabrication of graphene/polyaniline nanocomplex modified microbial fuel cell anodes. J Power Sour 224:139–144. https://doi.org/10.1016/j.jpowsour.2012.09.091
148. Jiang D, Li B (2009) Novel electrode materials to enhance the bacterial adhesion and increase the power generation in microbial fuel cells (MFCs). Water Sci Technol 59:557–563. https://doi.org/10.2166/wst.2009.007
149. Nourbakhsh F, Mohsennia M, Pazouki M (2017) Nickel oxide/carbon nanotube/polyaniline nanocomposite as bifunctional anode catalyst for high-performance Shewanella-based dual-chamber microbial fuel cell. Bioprocess Biosyst Eng 40:1669–1677. https://doi.org/10.1007/s00449-017-1822-y
150. Pareek A, Sravan JS, Mohan SV (2019) Fabrication of three-dimensional graphene anode for augmenting performance in microbial fuel cells. Carbon Resour Convers 2:134–140. https://doi.org/10.1016/j.crcon.2019.06.003
151. Nancharaiah YV, Mohan SV, Lens PNL (2015) Metals removal and recovery in bioelectrochemical systems: a review. Bioresour Technol 195:102–114. https://doi.org/10.1016/j.biortech.2015.06.058
152. Abbas SZ, Rafatullah M, Ismail N, Lalung J (2014) Isolation, identification, characterization, and evaluation of cadmium removal capacity of enterobacter species. J Basic Microbiol 54:1279–1287. https://doi.org/10.1002/jobm.201400157
153. Abbas SZ, Rafatullah M, Ismail N, Nastro RA (2017) Enhanced bioremediation of toxic metals and harvesting electricity through sediment microbial fuel cell. Int J Energy Res 41:2345–2355. https://doi.org/10.1002/er.3804

154. Zhang B, Feng C, Ni J, Zhang J, Huang W (2012) Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J Power Sour 204:34–39. https://doi.org/10.1016/j.jpowsour.2012.01.013
155. Qiu R, Zhang B, Li J, Lv Q, Wang S, Gu Q (2017) Enhanced vanadium (V) reduction and bioelectricity generation in microbial fuel cells with biocathode. https://doi.org/10.1016/j.jpowsour.2017.05.099
156. Jiang Y, Ulrich AC, Liu Y (2013) Coupling bioelectricity generation and oil sands tailings treatment using microbial fuel cells. Bioresour Technol 139:349–354. https://doi.org/10.1016/j.biortech.2013.04.050
157. Habibul N, Hu Y, Sheng GP (2016) Microbial fuel cell driving electrokinetic remediation of toxic metal contaminated soils. J Hazard Mater 318:9–14. https://doi.org/10.1016/j.jhazmat.2016.06.041
158. Fang Z, Song HL, Cang N, Li XN (2015) Electricity production from Azo dye wastewater using a microbial fuel cell coupled constructed wetland operating under different operating conditions. Biosens Bioelectron 68:135–141. https://doi.org/10.1016/j.bios.2014.12.047
159. Kawale HD, Ranveer AC, Chavan AR (2017) Electricity generation from wastewater using a microbial fuel cell by using mixed bacterial culture. J Biochem Technol 7:1123–1127
160. Kabutey FT, Ding J, Zhao Q, Antwi P, Quashie FK, Tankapa V, Zhang W (2019) Pollutant removal and bioelectricity generation from urban river sediment using a macrophyte cathode sediment microbial fuel cell (mSMFC). Bioelectrochemistry 128:241–251. https://doi.org/10.1016/j.bioelechem.2019.01.007
161. Marks S, Makinia J, Fernandez-Morales FJ (2019) Performance of microbial fuel cells operated under anoxic conditions. Appl Energy 250:1–6. https://doi.org/10.1016/j.apenergy.2019.05.043
162. Abbas SZ, Rafatullah M, Ismail N, Syakir MI (2017) A review on sediment microbial fuel cells as a new source of sustainable energy and heavy metal remediation: mechanisms and future prospective. Int J Energy Res 41:1242–1264. https://doi.org/10.1002/er.3706
163. Chuo SC, Mohamed SF, Setapar SHM, Ahmad A, Jawaid M, Wani WA, Yaqoob AA, Ibrahim MNM (2020) Insights into the current trends in the utilization of bacteria for microbially induced calcium carbonate precipitation. Material 13:4993
164. Abbas SZ, Rafatullah M, Ismail N, Syakir M (2018) The behaviour of membrane less sediment microbial fuel cell in the terms of bioremediation and power generation
165. Yang W, Ogan BL (n.d.) Immobilization of a metal-nitrogen-carbon catalyston activated carbon with enhanced cathode performance in microbial fuel cells. https://doi.org/10.1002/cssc.201600573
166. Liu Y, Fan YS, Liu ZM (2019) Pyrolysis of iron phthalocyanine on activated carbon as highly efficient non-noble metal oxygen reduction catalyst in microbial fuel cells. Chem Eng J 361:416–427. https://doi.org/10.1016/j.cej.2018.12.105
167. Nguyen D-T, Taguchi K (2019) A disposable water-activated paper-based MFC using dry E. coli biofilm. BiochemEng J 143:161–168
168. Zhang Y, Mo G, Li X, Zhang W, Zhang J, Ye J, Huang X, Yu C (2011) A graphene modified anode to improve the performance of microbial fuel cells. J Power Sour 196:5402–5407. https://doi.org/10.1016/j.jpowsour.2011.02.067
169. Yang Y, Lin E, Sun S, Chen H, Chow A (2019) Direct electricity production from subaqueous wetland sediments and banana peels using membrane-less microbial fuel cells. Ind Crops Prod 128:70–79
170. Abourached C, Catal T, Liu H (2014) Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Res 51:228–233. https://doi.org/10.1016/j.watres.2013.10.062
171. Wang Z, Zhang B, Jiang Y, Li Y, He C (2018) Spontaneous thallium (I) oxidation with electricity generation in single-chamber microbial fuel cells. Appl Energy 209:33–42. https://doi.org/10.1016/j.apenergy.2017.10.075
172. Tao HC, Li W, Liang M, Xu N, Ni JR, Wu WM (2011) A membrane-free baffled microbial fuel cell for cathodic reduction of Cu(II) with electricity generation. Bioresour Technol 102:4774–4778. https://doi.org/10.1016/j.biortech.2011.01.057

173. Yun-Hai W, Bai-Shi W, Bin P, Qing-Yun C, Wei Y (2013) Electricity production from a bio-electrochemical cell for silver recovery in alkaline media. Appl Energy 112:1337–1341. https://doi.org/10.1016/j.apenergy.2013.01.012
174. Singhvi P (2013) Simultaneous chromium removal and power generation using algal biomass in a dual chambered salt bridge microbial fuel cell. J BioremedBiodegrad 04. https://doi.org/10.4172/2155-6199.1000190
175. Tao HC, Liang M, Li W, Zhang LJ, Ni JR, Wu WM (2011) Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. J Hazard Mater 189:186–192. https://doi.org/10.1016/j.jhazmat.2011.02.018
176. Ryu EY, Kim M, Lee S-J (2011) Characterization of microbial fuel cells enriched using Cr(VI)-containing sludge. J Microbiol Biotechnol 21:187–191. https://doi.org/10.4014/jmb.1008.08019
177. Wu Y, Wang L, Jin M, Kong F, Qi H, Nan J (2019) Reduced graphene oxide and biofilms as cathode catalysts to enhance energy and metal recovery in microbial fuel cell. Bioresour Technol 283:129–137. https://doi.org/10.1016/j.biortech.2019.03.080
178. Xafenias N, Zhang Y, Banks CJ (2013) Enhanced performance of hexavalent chromium reducing cathodes in the presence of Shewanella oneidensis MR-1 and Lactate. Environ Sci Technol 47:4512–4520. https://doi.org/10.1021/es304606u
179. Choi C, Hu N (2013) The modeling of gold recovery from tetrachloroaurate wastewater using a microbial fuel cell. https://doi.org/10.1016/j.biortech.2013.01.143
180. Li F, Jin C, Choi C, Lim B (2019) Simultaneous removal and/or recovery of Cr(VI) and Cr(III) using a double MFC technique. Environ EngManag J 18:235–242. https://doi.org/10.30638/eemj.2019.023
181. Huang L, Li T, Liu C, Quan X, Chen L, Wang A, Chen G (2013) Synergetic interactions improve cobalt leaching from lithium cobalt oxide in microbial fuel cells. Bioresour Technol 128:539–546. https://doi.org/10.1016/j.biortech.2012.11.011
182. Chen B-Y, Wang Y-M, Ng I-S (2011) Understanding interactive characteristics of bioelectricity generation and reductive decolorization using Proteus hauseri. Bioresour Technol 102:1159–1165. https://doi.org/10.1016/j.biortech.2010.09.040
183. Solanki K, Subramanian S, Basu S (2013) Microbial fuel cells for azo dye treatment with electricity generation: a review. Bioresour Technol 131:564–571. https://doi.org/10.1016/j.biortech.2012.12.063
184. Li Z, Zhang X, Lin J, Han S, Lei L (2010) Azo dye treatment with simultaneous electricity production in an anaerobic-aerobic sequential reactor and microbial fuel cell coupled system. Bioresour Technol 101:4440–4445. https://doi.org/10.1016/j.biortech.2010.01.114
185. Liu Y, Song P, Gai R, Yan C, Jiao Y, Yin D, Cai L, Zhang L (2019) Recovering platinum from wastewater by charring biofilm of microbial fuel cells (MFCs). J Saudi Chem Soc 23:338–345. https://doi.org/10.1016/j.jscs.2018.08.003
186. Khan MZ, Singh S, Sultana S, Sreekrishnan TR, Ahammad SZ (2015) Studies on the biodegradation of two different azo dyes in bioelectrochemical systems. New J Chem 39:5597–5604. https://doi.org/10.1039/C5NJ00541H
187. Ding H, Li Y, Lu A, Jin S, Quan C, Wang C, Wang X, Zeng C, Yan Y (2010) Photocatalytically improved azo dye reduction in a microbial fuel cell with rutile-cathode. Bioresour Technol 101:3500–3505. https://doi.org/10.1016/j.biortech.2009.11.107
188. Mu Y, Rabaey K, Rozendal RA, Yuan Z, Keller J (2009) Decolorization of Azo dyes in bioelectrochemical systems. Environ Sci Technol 43:5137–5143. https://doi.org/10.1021/es900057f
189. Sun J, Bi Z, Hou B, Cao YQ, Hu YY (2011) Further treatment of decolorization liquid of azo dye coupled with increased power production using microbial fuel cell equipped with an aerobic biocathode. Water Res 45:283–291. https://doi.org/10.1016/j.watres.2010.07.059
190. Sun J, Li Y, Hu Y, Hou B, Xu Q, Zhang Y, Li S (n.d.) Enlargement of anode for enhanced simultaneous azo dye decolorization and power output in air-cathode microbial fuel cell. https://doi.org/10.1007/s10529-012-1002-8

191. Yu F, Wang C, Ma J (2016) Applications of graphene-modified electrodes in microbial fuel cells. Materials (Basel) 9. https://doi.org/10.3390/ma9100807
192. Oon YL, Ong SA, Ho LN, Wong YS, Dahalan FA, Oon YS, Lehl HK, Thung WE, Nordin N (2018) Up-flow constructed wetland-microbial fuel cell for azo dye, saline, nitrate remediation and bioelectricity generation: from waste to energy approach. Bioresour Technol 266:97–108. https://doi.org/10.1016/j.biortech.2018.06.035
193. Abbas SZ, Rafatullah M, Ismail N, Shakoori FR (2018) Electrochemistry and microbiology of microbial fuel cells treating marine sediments polluted with heavy metals. https://doi.org/10.1039/c8ra01711e
194. Kumar R, Singh L, Zularisam AW, Hai FI (2018) Microbial fuel cell is emerging as a versatile technology: a review on its possible applications, challenges and strategies to improve the performances. Int J Energy Res 42:369–394. https://doi.org/10.1002/er.3780
195. Zhou M, Chi M, Luo J, He H, Jin T (2011) An overview of electrode materials in microbial fuel cells. J Power Sour 196:4427–4435. https://doi.org/10.1016/j.jpowsour.2011.01.012
196. Do MH, Ngo HH, Guo WS, Liu Y, Chang SW, Nguyen DD, Nghiem LD, Ni BJ (2018) Challenges in the application of microbial fuel cells to wastewater treatment and energy production: a mini review. Sci Total Environ 639:910–920. https://doi.org/10.1016/j.scitotenv.2018.05.136

Graphene Derived Electrode Materials for Microbial Fuel Cell

K. Senthilkumar, L. Dharani, J. Jayabharathi, M. Naveenkumar, and N. Pooja

1 Introduction

Microbial Fuel Cell (MFC) is a significant technology that aides in the mitigation of climate change by generation of bioenergy. Fossil fuel depletion, as well as environmental concerns for-example acid rain, greenhouse gas emissions, and global warming, have prompted the growth of substitute energy sources like MFC. MFC's, in particular, are being investigated as an alternate option due to their remarkable ability to produce energy while also removing contaminants. Wastewater treatment, removal of toxic compounds, heavy metal remediation from soil and water, and biogas production are the most typical applications of MFC [1]. The beginning of MFC can be dated back to 1911, when Potter obtained 0.3–0.5 V when working with a platinum electrode put into a liquid solution of yeast and Escherichia coli using a glucose medium. MFC first came to prominence in the 1950s, when researchers

K. Senthilkumar (✉) · J. Jayabharathi
Department of Chemical Engineering, Kongu Engineering College, Erode, Tamilnadu, India
e-mail: uksen2003@gmail.com; senthilkumar.chem@kongu.ac.in

J. Jayabharathi
e-mail: jaya.chem@kongu.ac.in

L. Dharani
Department of Chemical Engineering, KPR Institute of Engineering and Technology, Coimbatore, India

M. Naveenkumar (✉)
Department of Civil Engineering, IFET College of Engineering, Villupuram, India
e-mail: er.naveenmanick@gmail.com

N. Pooja
Department of Chemical Engineering, Central Institute of Petrochemicals Engineering & Technology, Chennai, Tamilnadu, India

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_7

were looking for a new way to convert human waste to electricity in a timely manner during space missions. Redox-active mediators were commonly utilized in MFC's until the 1980s, and they considerably increased the power density output of MFC's. The practicality of MFC's as modest power supply increased at this point, and more scientists got keen on the innovation work of MFC in relation to alternate renewable energy systems [2].

A conventional MFC system has anode part and cathode part divided by membrane as shown in Fig. 1. The MFC works on the basis that it is a device that converts substrates directly into electricity through substrate oxidation, with exoelectrogenic microbes acting as a biocatalyst. When bacteria oxidize organic and inorganic materials, they produce electrons and protons, which generate electricity. Electrons created by microorganisms on these substrates go through the conductive material to the anode and cathode, leading in power production. The H^+ ions produced by bacteria in the anode flow through the semi permeable membrane to the cathode as a result of electrochemical gradient. Pure water is formed when electrons combine with H^+ ions and oxygen in cathode part. Figure 1. illustrates the schematic representation of MFC, which is made up of anode and cathode part separated by membrane.

The overall process involves the decomposition of the substrate into carbon dioxide and water, as well as the creation of energy as a byproduct. The MFC can produce electron from the anode with substrate oxidation by microorganisms and passed to the cathode part through electrical device connected in externally using the electrode reaction pair described above. The nature of the microbes and operational variables such as conductivity, surface area of electrodes, temperature, membrane, and pH are having significant collision on MFC performance.

A big electrode surface area, good electrical conductivity, excellent stability, and cheap are all important qualities of electrode materials in MFC performance. MFC

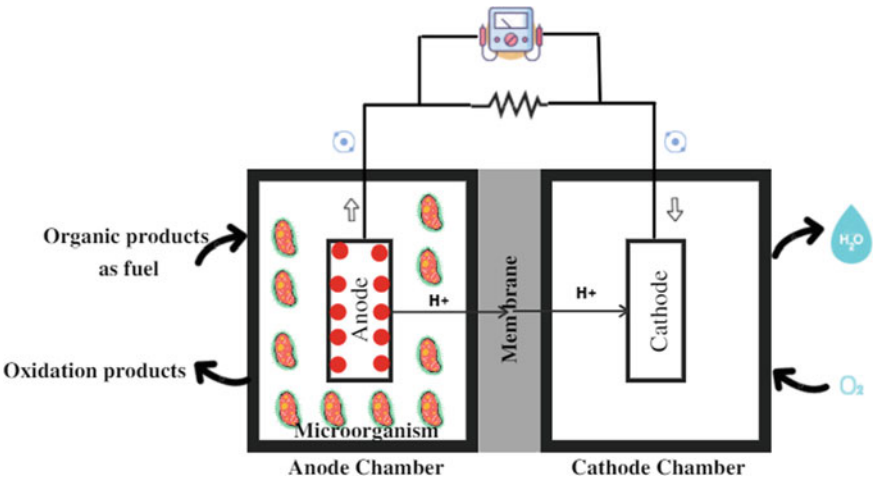

Fig. 1 Schematic representation of double chambered MFC

uses a wide range of anode and cathode materials. Stainless Steel (SS), titanium plate, SS scrubber, SS mesh, brass, silver, nickel, copper, and gold sheets are the most often used metal electrodes. Metal electrodes offer a high electrical conductivity; however, they tend to raise the MFC's cost [3]. The use of expensive, poisonous, and dangerous chemical agents as electrode material is a fundamental flaw in present laboratory scale MFC research [4]. Researchers recently discovered that employing graphene modified materials used as electrodes, which are extra conductive and structurally steady with a greater surface area and greater electrocatalytic activity than standard electrode materials, improved the MFC's performance. The MFC power density was also found to have noticeably improved due to increased catalyst dispersion on the graphene surface [5]. As a result, graphene-derived electrode materials appear to be a superior alternative to standard electrode materials, increasing overall MFC efficiency.

2 An Overview of Conventional Electrode Materials Used in MFC

In MFC, several electrode materials have been used for power production shown in Table 1. The electrode materials have a big collision on the MFC's performance and cost. The anode material in MFC's not only serves as a conductor, as it does in typical fuel cells, but it also provides assist for biofilms formation. So it might be compatible with bacteria exist [6]. There exist not many contrasts in the terminal material choice of anode and cathode, in any case both electrodes have properties like surface area, conductivity, stability and durability, porosity, and cost and accessibility. The most generally utilized customary MFC electrode materials are as follows.

Table 1 Various MFC electrode materials and their related energy output

Anode material	Cathode material	Energy output	Reference
Carbon cloth	Carbon felt	468 mW m^{-2}	Hou et al. [8]
Carbon paper	Carbon paper	142 mW m^{-2}	Zhao et al. [9]
Platinum loaded carbon cloth	Carbon paper	38 mW m^{-2}	Min et al. [10]
Carbon felt	Activated carbon, carbon black and poly binder	680–820 mW m^{-2}	Kim et al. [11]
Graphite felt	Graphite felt	0.57 mA m^2	Chaudhuri and Lovely [12]
Titanium oxide composite coated on to carbon paper	Carbon paper	1060 mW m^{-2}	Zhao et al. [13]

2.1 Carbon Cloth

Carbon cloth is an anode material that is extensively utilized in BES due to its unique qualities, which include huge surface area, high porosity, strong conductivity, and the capacity to build 3D structures with good flexibility and high mechanical strength. Carbon fabric is made from the thermal decomposition of acrylic and consists of long individual carbon fibers with diameters ranging from 5 to 7 μm. These individual strands are bundled together and then woven together to create the carbon cloth [7]. The main drawback is the possible high cost of carbon cloth, which, when compared to other carbon-based electrode materials, is quite cheap.

2.2 Carbon Brush

Carbon brush is a fascinating material made of twisted carbon fibers around a titanium core. Its most commonly used surface area is relatively large, and the area to volume ratio is ideal. The central titanium metal ensures the excellent electrical conductivity while also increasing the material cost. The limitation of carbon brush includes their high cost, and continuous research is aimed at lowering overall cost.

2.3 Carbon Paper

Carbon paper is a planar carbonaceous substance that is moderately permeable yet also expensive and weak, with most demonstrations taking place in a lab setting in batches.

2.4 Carbon Veil

The single layer of carbon veil is very delicate, because the material is adaptable; it very well may be collapsed to shape a robust and porous 3-D terminal. It is a cost effective substance with a good porosity and relatively greater conductivity. The latter is critical for bacteria to be able to approach and conquer all accessible material sites.

2.5 Carbon Mesh

Carbon mesh is another material that is monetarily accessible, cheap and has a poor conductivity. The principle issue is less mechanical strength, which could prompt less sturdiness under high stream environment. Carbon mesh can likewise be folded to make a three-dimensional electrode, yet its porosity is poor.

2.6 Granular Activated Carbon (GAC)

GAC is popular anode material mainly used for its biocompatibility and low cost. Because of its porous form, it has a limited electrical conductivity. GAC is employed as a packing material rather than a freestanding anode because of this disadvantage. Because of the nanoscale pore size of GAC, its great surface area availability cannot be efficiently utilized by bacteria.

2.7 Granular Graphite

Granular graphite has a high electrical conductivity and is more commonly employed as a packing material than as a stand-alone anode. Graphite has excellent electrochemical properties, and its biocompatibility has been established by Scanning Electron Microscopy (SEM), as evidenced by the plenty of a biofilm adhered to surface area of graphite electrode.

3 Non-carbon-Based Electrodes

In spite of the way that carbon-based anodes are the favored electrode in MFC setups because of their underlying flexibility, non-carbon-based terminals have likewise been utilized in MFC's. Anode and cathode electrodes made of non-carbon-based materials include stainless steel, platinum coated titanium metal, and uncoated titanium. According to findings, stainless steel gives greater current density (674 μA cm^{-2}) and nickel (384 μA cm^{-2}) respectively. Due to the production of metal oxides, which act as a barrier for charge transfer between the biofilm and the metal, non-noble metals like cobalt and titanium produced minimal current density.

3.1 Graphene Derived Electrode Materials Used in MFC

Graphene, the world's thinnest material, was discovered by Geim and Novoselov in 2004 [14]. Graphene's remarkable qualities, like its good electrical conductivity, ultrahigh specific surface area, exceptional mechanical resilience and flexibility, chemical inertness, and superior biocompatibility, open up new possibilities for MFC's [15]. During MFC operations, graphene has non-toxic impacts on bacterial growth. As a result, the toxicity of other materials, like copper, platinum, etc., can be greatly lowered by altering or combining it with other materials, like metal. The exceptional performance qualities of graphene-based electrodes outperform traditional carbon electrodes [16]. Because of its close physical proximity and advantageous electrical, mechanical, and physicochemical capabilities, graphene is becoming popular in the vitality domains. Its qualities are extremely encouraging and consistent, making it ideal for wide range of application like fuel cells, batteries, super capacitors, photo catalysts, and solar cells [17].

3.2 Graphene Structure

Graphene is a carbon allotrope that takes the shape of a 2D, atomic-scale hexagonal lattice with one atom forming each vertex due to sp^2 hybridization. Figure 2 shows the structure of single graphene sheet. The carbon atoms are organized in a honeycomb lattice. Each lattice has three bonds with strong connections, providing a sturdy hexagonal structure. Carbon atoms connect with adjacent carbon atoms in single layer graphene using sp^2 hybridization to form a benzene ring in which each atom provides an unpaired electron. Because of its closely packed carbon atoms and sp^2 orbital hybridization, a mixture of orbitals s, p_x, and p_y that make up the σ bond of graphene is extremely stable. The π-bond is formed by the final p_z electron. The π-band and π^*-bands are formed when the π-bonds combine. The distance between carbon–carbon bond is 0.142 nm. The bond between carbon atoms is strong enough to withstand external strain from a twisting lattice plane, preventing atom reconfiguration [18].

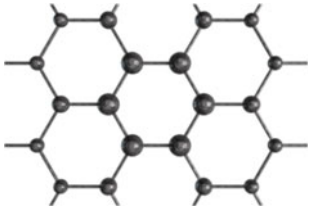

Fig. 2 Structure of single graphene sheet

3.3 Properties of Graphene

Graphene has several excellent qualities in terms of visual clarity, mechanical strength, thermal conductivity, and electric conductivity. Graphene has thickness range of 1/200,000th the dia of a human hair while on the other hand, has a very stable structure. It is made up of only one atomic layer of carbon atoms, which adds to its super thin and lightweight properties. Graphene with several layers would produce different colors and contrasts based on light refraction and interference, which might be used to discern the layers of graphene. Graphene has a good mechanical strength and high thermal conductivity. The fact that graphene is a zero-overlap semi-metal with very good conductivity is one of its most useful characteristics. Table 2 lists the most important graphene properties of graphene [18].

3.4 Graphene-Based Electrodes Synthesize

The fabrication of graphene-modified electrodes has received an interest due to graphene's attractive characteristics and exceptional shapes shown in Fig. 3. In numerous investigations, GO is always used as a forerunner to create graphene and its compounds. Electrochemical reduction, layer-by-layer (LBL) self-assembly, Bio-reduction, Chemical Vapour Deposition (CVD), Direct deposition, and chemical doping are all common methods for fabricating Gr-based electrodes. This section briefly discusses the various categories of synthesis procedures for graphene-altered electrodes in MFC's.

Table 2 Properties of graphene

Properties	Value
Thickness	0.35 nm
Planar density	0.77 mg/m^2
Area of a graphene unit structure	0.052 nm^2
Transparency	97.7%
Conductivity	10^6 S/m
Sheet resistance	31 Ω/sq
Mobility	2 * $10^5 cm^2$/Vs
Tensile strength	125 Gpa
Elastic modulus	1.1 Tpa
Strength	42 N/m
Thermal conductivity	5×10^3 W/mK
Specific surface area	2630 m^2
Mechanical strength	1060 Gpa
Young's modulus	TPa

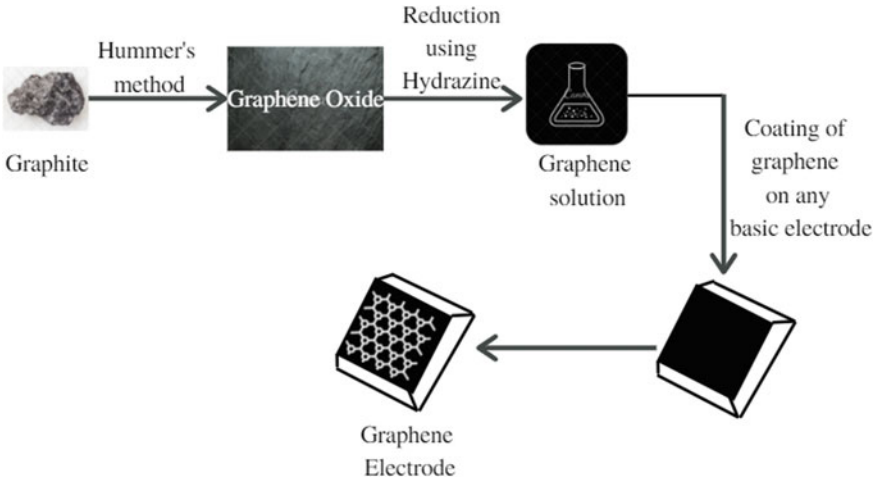

Fig. 3 Synthesize of graphene altered electrode for application in MFC

3.4.1 Direct Deposition

The direct deposition method of fabricating graphene-derived electrodes entails three steps. The first step employs hummer's method to chemically exfoliate graphite and obtain Graphene Oxide (GO). The next step is to use a reducing agent, such as hydrazine, to convert GO to graphene (Gr). The final steps involve coating the arranged graphene on any fundamental electrode such as SS mesh, fiber, and so on using a simple immersion method [19].

3.4.2 Electrochemical Reduction

Another strategy for manufacture is the electrochemical reduction of GO to Gr, which can be done directly from GO nano-sheets organized on the surface of electrode from a solution of dispersed GO nano-sheets. Accordingly, the thickness of the resulting layer can be controlled, replicated, and homogenous without the use of harmful chemicals. Carbon materials, conductive polymers, or their monomers, such as multi-walled carbon nanotubes (CNT's), Poly (3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), or polypyrrole (PPy), could then be placed over the Gr coated electrode using chronoamperometry [19]. Figure 4 depicts the electro-polymerization with graphene.

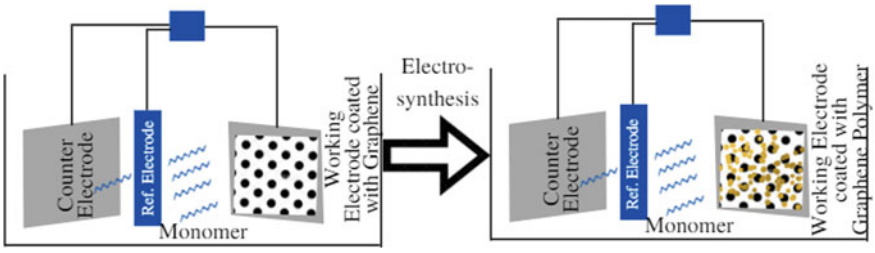

Fig. 4 Electro-polymerization with graphene

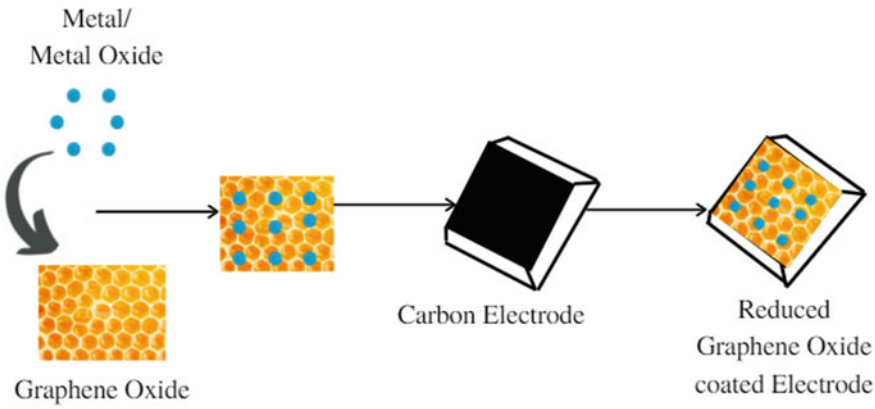

Fig. 5 Graphene oxide hybrid electrode materials using LBL self-assembly technique

3.4.3 Self-Assembly Methods

This is one of the technique in which essential components in a solution, such as molecules, nanomaterials, and big size objects, impulsively form an efficient and constant structure. The gelation procedure is one of the most prevalent methods for producing 3D graphene (3DG) from GO sheets in homogenous liquids. Many approaches, such as altering the pH value of the GO solution, adding cross linking agents, or employing chemical reduction processes, can cause the suspension of GO sheets to gel. There are a variety of ways to make graphene sheets from GO sheets suspended in electrostatic contact utilizing various self-assembly mechanisms. The major self-assembly strategy for synthesizing homogeneous nanostructure films is layer-by-layer (LBL) assembly as shown in Fig. 5.

3.4.4 Bio-reduction

Bacteria can self-assemble utilizing water soluble GO in the Bio-reduction method, which causes in-situ bio-reduction of non-conductive GO to conductive rGO,

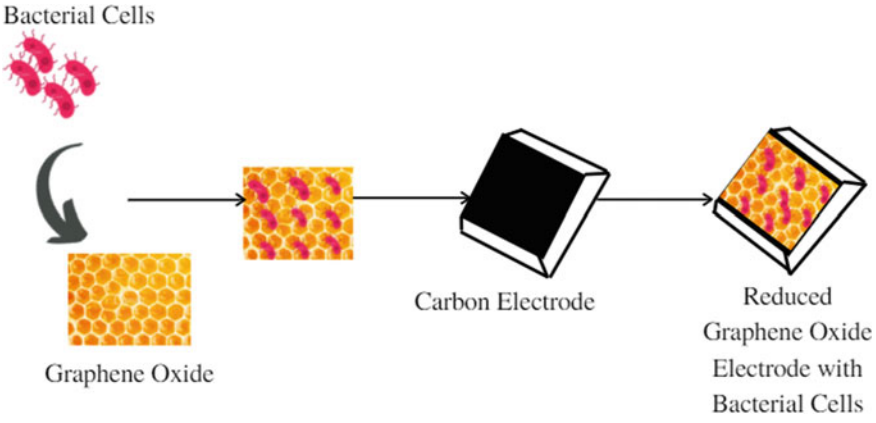

Fig. 6 Bio-reduction of bacterial cells on graphene derived electrode

resulting in a three-dimensional (3D) self-assembled biofilm. When GO solution was given to the anode compartment of a dual chamber MFC, the anolyte turned black with the formation of aggregates, meaning that the water dispersible brown GO was converted to the water precipitated black rGO. Figure 6 shows the bio-reduction of bacterial cells on graphene derived electrode.

3.4.5 Chemical Vapour Deposition (CVD)

CVD is a commonly used process for creating semiconductor films in which a carbon source undergoes a chemical reaction at a high temperature with a high gas flow rate, and the resultant film is deposited on the surface of a heated solid substrate. Figure 7 shows the CVD method of fabricating graphene derived electrodes. Transition metal compounds, such as Cu and Ni, are the most common graphene substrates. The graphene films that have been created can be transferred to different surfaces while

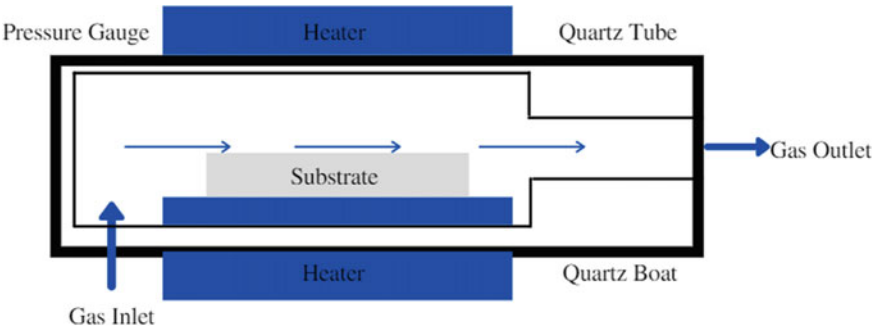

Fig. 7 Chemical vapour deposition method of fabricating graphene derived electrodes

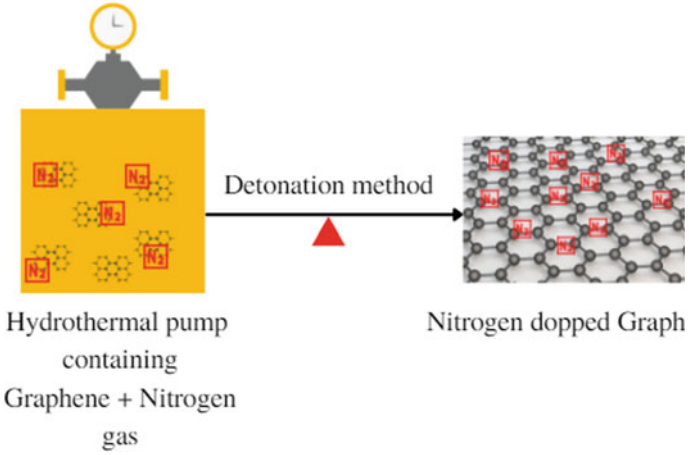

Fig. 8 Schematic of nitrogen doped graphene

retaining their high conductivity and transmittance. This technique can produce large-area, high-quality graphene, but its high cost and complexity prevents it from being used in big-scale applications. Substrate is one of the influenced factors to produce the quality of graphene.

3.4.6 Chemical Doping

Heteroatoms can be chemically doped into graphene. This method is efficient adequate to optimize graphene's physical and chemical properties. Doping Gr with nitrogen (N) atoms was recently investigated as a viable method for increasing its conductivity, resulting in novel nano-materials. The observed increase in electro-catalytic activity of N-doped Gr in basic solution has extraordinary potential as a metal-free catalyst in fuel cells, in which N molecules activate charge delocalization on the carbon design and increase the openness of the edge plane to sustain catalytic activity extraordinarily [20]. Figure 8 illustrates the N doped graphene structure.

In addition to the methods outlined above, spraying, explosion, electrostatic interaction, electrophoresis, the explosion method and other processes can be employed to produce graphene-modified electrodes.

4 Graphene-Based Anode Materials

The anode material, which is aligned with bacterial adhesion and electron transfer from microbes to the electrode via various mechanisms, has a strong influence on the power density of MFC. A bio-anode should be biocompatible and also have a

Table 3 Summary of graphene derived anode electrode materials used in MFC

Anode electrode	Modified anode electrode	Cathode electrode	Power density (mW m^{-2})
3D GF	PANI	Carbon cloth	768
Graphite felt	PPy/GO	Carbon Felt	1326
Graphite block	Graphene	Carbon paper	102
Glassy carbon	Microbially reduced graphene	Carbon cloth/Pt	1905
Carbon cloth	Graphene	Carbon cloth	52.5
Nickel foams	Graphene/TiO_2	Carbon paper	1060
Carbon paper	Graphene/Au	Carbon paper	508
Carbon cloth	PANI-rGO	Carbon felts	1390
Carbon cloth	TiO_2/rGO	Carbon fibre brush	3169
Carbon cloth	Graphene	Carbon cloth	2850

large specific surface area to support a large number of microbes. Graphene-based materials are gaining significance for extremely efficient MFC anodes in this regard [21]. Zhang and colleagues reported that a dual-chamber MFC with a graphene altered stainless-steel mesh (GMS) anode electrode performed better electrochemically. Thereafter, a 3D macro porous anode with graphene coating on stainless steel fiber felts (SSFF's) were proven to induce a maximum power density of 2,142 mW m^{-2} in MFC, substantially outperforming the unmodified SSFF-MFC. Graphene-modified carbon cloth (CC) electrodes have a maximum power density than bare CC, activated carbon, or bare graphite altered electrodes, according to certain research shown in Table 3. Three-dimensional (3D) anodes made from graphene sponge (GS) provided a huge area for microbial colonization in a 3D open space. Microorganisms covered the GS surface, which were connected by microbial nanowires, giving a likely direct conduit for extracellular electron transfer. This highly porous graphene sponge ensures its prospective use in MFC's as a flexible anode material. The greatest power density obtained from the 3D graphene/PANI MFC (768 mW m^{-2}) was almost four times greater than that obtained from the carbon cloth MFCs (158 mW m^{-2}), according to a macro porous and monolithic MFC anode based on PANI hybridized 3D-graphene. A novel 3D chitosan/vacuum-stripped graphene (VSG) scaffold with hierarchically porous structure offered an open space in the anode interior for bacteria colonization and improved the affinitive contact between multilayered bacteria and biocompatible VSG, resulting in a remarkable 78-fold increase in powder density. The BET surface area of a nanocrystal TiO_2/rGO hybrid (324.7 m^2 g^{-1}) was large. It was discovered that a nanocrystal TiO_2/rGO hybrid with numerous mesopores had a greater specific surface area, which was useful to achieving superior electrocatalytic performance.

5 Graphene Derived Cathode Materials

The maximum power output of MFC influenced by the oxygen reduction reaction (ORR) in the cathode chamber. Because of its modest over potential, platinum (Pt) is forever utilized as a catalyst in the cathode process, but it is expensive and limited its use in industrial scale applications. The reduction pathways are strengthened by graphene altered materials, which give a high number of potential active sites [22]. Polymers, metal-based materials are embedded on the surface of graphene, were found to improve ORR activity by means of ever-increasing the active sites of the graphene nanosheets, according to studies. Except in MFC's that use aerobic microorganisms as electron acceptors, no microbes adhered to the electrode surface in comparison to the anode electrode. As a result, improving the surface modification of the electrodes is the recommended way for increasing electrical conductivity. Furthermore, the cost of producing graphene sheets in large quantities is far cheaper than that of CNT's. As a result, much work has gone into developing graphene as a catalyst support for fuel cell applications. The addition of nitrogen atoms (NG) to graphene results in a high electrocatalytic activity for ORR in an alkaline solution, suggesting that it could be used as a cathode catalyst in fuel cells. The greatest power density attained when NG was used as the cathode catalyst in MFC's was comparable to that of typical Pt/C catalysts. More notably, NG-based MFC's produced more stable power than Pt-based MFC's. Figure 4 depicts the graphene modified cathode electrode materials used in MFC (Table 4).

Table 4 Summary of graphene derived cathode electrode materials used in MFC

Cathode electrode	Modified cathode electrode	Anode electrode	Power density mW m^{-2}
Carbon paper	NG	Carbon cloth	764–788
Glassy carbon	Fe- and N-functionalized graphene	Carbon felt	885
Carbon paper	MnO_2-NTs/graphene	Carbon cloth	4.68 Wm^{-3}
Carbon cloth	Pt–Co/G	Carbon cloth	1378
Carbon cloth	Graphene/biofilm	Carbon cloth	302.2–344.2
Carbon cloth	NG	Carbon felt brush	1335–1365
Stainless steel net	NG	Carbon brush	1159.34
Carbon paper	Fe-NG	Carbon felt	1149.8
Carbon cloth	α-MnO_2/GO	Carbon cloth	3359
Stainless steel mesh	Cobalt sulfides/GO	Graphite fibre	1138–1744

6 Pros and Cons of Graphene Derived Electrodes

The huge demand for storage devices has led to increased research in exploring materials of unique properties which can exhibit high performance. Graphene has been identified as one of such materials exhibiting promising results. Graphene is one of largest among aromatic molecules, belonging to the category of polycyclic aromatic hydrocarbons. Many carbon allotropes use its basic structure for formation of graphite, carbon nano tubes, and charcoal. The research works on graphene indicate that it is a promising conducting substance for the upcoming storage equipment. Graphene has several inherent properties that make it an appropriate substance for different real field applications in different sectors of industry. This strongest material possesses high mechanical resistance, larger surface area, superior electrical, and heat conductivity, which makes it the most suitable material for fuel cells and capacitors. When used as electrodes, graphene can be used as a composite and support material. Improved electrode efficiency is generally observed when graphene is used as a support material because it maintains metal ions in regular order.

When graphene is used as a composite material in electrodes, it facilitates the charge, and its performance is ensured by its well—ordered structure and higher conductivity. In general carbon materials possess low density of pores and also low storage density of carbon content electrode resulting in low volume energy density. Since, graphene is a carbon material, it also faces the similar problem, and hence it has been proposed to develop a controlled combination of graphene with other materials for electrode structure design resulting in graphene-based electrodes with high density. Conductive agents or binder are not contained in most of the graphene-based electrodes further improving volume energy density. Promising results were obtained when analyzing graphene-based materials, and there are huge opportunities and challenges in synthesizing and using graphene-based electrode materials. It is one of potential electrode materials for electrochemical energy storage. Because of its appreciable conductivity stable physical structure and large surface area, graphene is the most appropriate material for the majority of the electrochemical energy storage equipment's.

In certain applications, the 2D layered structure is constructed into 3D structures, with adjustments in pore structure. Owing to its unique properties, graphene is used in combination with other materials in applications like lithium-ion batteries, lithium oxygen batteries, and lithium sulphur batteries, higher performance was observed in these applications.

In lithium-ion batteries, graphene is added to electrode formulations to improve the performance. This organic-based electrode overcomes the limitations in surface area, capacitance, and conductivity of inorganic-based electrodes. Graphene is one of the best materials owing to its versatility, which enables it to overcome conventional battery limitations when used in cathode electrode formulations. In electrodes constituted of graphene and metal oxide hybrids, the primary cathode material used is the graphite, which has the ability to store the lithium ions by the process of surface adsorption and also there occurs bonding due to its large surface area.

The downsides of conventional metal oxides used in batteries such as low conductivity, energy density, and loss of contact points are eliminated when used with graphene. The hybrid structure improves greater interaction between the hybrid matrix and the interstitial ions which increases the conductivity of the structure. In the synthesis of graphene—MO structure, graphene with its regular repeating structure acts as a template and produces a uniformly distributed matrix. MO nanoparticle aggregation is largely limited resulting in larger surface area for charge and discharge cycles. As a whole there is a large improvement in the cyclic performance and specific capacity when compared to traditional pure MO electrodes. In first 10 cycles, these hybrid electrodes can exhibit up to 1100 $mAhg^{-1}$. Apart from hybrid electrodes, electrodes made of graphene and carbon nanotubes or fullerenes have also been synthesized and used currently. Dispersing the graphene sheets with either fullerenes or carbon nanotubes increases the inter-graphene spacing, thus increasing the home for more lithium ions resulting increased specific capacity to around 40%. Graphene enhances the performance of Graphene Lithium Sulphur Batteries. Here the sulphur ions are supported by graphene, because of which major problems like less utilization of sulphur cathode and inorganic salt deposition on the cathode are eliminated. High energy sodium-sulphur batteries used at room temperature are also found to use graphene-sulphur composites as electrodes. Graphene-based composites are used as electrocatalyst in zinc-air batteries making it highly efficient. In wholesome, graphene has several other advantages when used in the synthesis of electrodes, which are listed below.

- Thinnest material with pliable and transparent single layer of carbon atoms.
- Incredibly flexible material stronger than steel.
- Higher potential to transfer electrons at a very faster rate compare at the speed of 1000 km /s.
- Superior conduction of heat and electricity.
- Provides faster technological changes for its usage in the production of high speed electronic devices.
- Highly efficient sensors in detecting explosives.
- Storing hydrogen for fuel cell powered cars.

Despite its remarkable advantages and applications, graphene also possess various disadvantages.

- It does not possess band gap; research works have been undertaken in this regard.
- It is susceptible to oxidative environments
- It is synthesized using toxic chemicals in high temperatures; hence, it exhibits toxic qualities which is one of the major limitations in certain applications.
- The practical application of it is not completely recognized; hence, more research is required.
- High quality grapheme materials are expensive, and also the process of synthesis is expensive.
- It is a non-renewable resource and also harder to synthesize.

- It has lesser actual strength than the intrinsic strength.
- There is no control over the size of the graphene sheet produced.
- It is not stable below the size of 20 nm.

7 Applications of Graphene Derived Electrodes

Graphene is extensively utilized electrode material in batteries, light-emitting diodes, transistors, solar cells, and other flexible devices. Some of the applications of graphene are discussed below. Mohammad et al. [22] examined usage of graphene for ultra-lightweight photovoltaics. So as to improve the electrical properties, they employed a roll-to-roll (R2R) transfer technique. It was done on flexible substrates with parylene as an interfacial layer. By the process of chemical vapor deposition a layer of parylene is deposited on graphene-copper foils and then laminated onto ethylene vinyl acetate. Later the samples are then delaminated from the copper using an electrochemical transfer process which resulted in flexible conductive substrates. The results of characterization techniques indicated that the parylene C and D doped graphene had higher carrier density due to the embedded chlorine atoms in the structure. Calculations of density functional theory indicated that the binding energy between graphene and parylene is stronger than the binding energy of EVA and graphene. It resulted in less tear in the graphene during R2R transfer. It is then followed by the fabrication of organic solar cells on ultrathin flexible parylene/graphene substrates. The power conversion efficiency achieved was of 5.86% [22]. Hanrui Su and Yun Hang Hu summarized the applications of graphene-based materials used in fuel cells. When compared with the commercial Pt/C catalyst, heteroatom-doped graphene indicated high electroactivity. Many anchoring sites were provided by doped graphene and rGO for the active metal particles which made the dispersion uniform. Various electrochemical reactions such as ORR, EOR, MOR, and FAOR are supported by the high surface area and electrical conductivity of the graphene-supported catalysts. Long term stability was ensured by the strong metal-graphene interaction. In order to enhance active sites, three dimensional graphene electrodes were also developed, in order to enhance and reduce the diffusion resistance. Graphene and graphene oxide are also found to exhibit high proton conductivity and less permeation of fuel. This enabled them to act as alternative electrolyte material. Graphene which is highly conductive and chemically stable also found to protect metallic plates from corrosion [23]. Syama and Mohanan inferred that graphene is ideal for photo thermal therapy due to its high near-IR absorbance. Hence the multifunctional graphene was found to be a reliable material for the diagnosis and treatment. By interacting with the cell membrane, it also exhibits the antibacterial property. Graphene also has potential application in tissue regeneration because of its nature of attachment and proliferation of the stem cells and neuronal cells. 3D Structure is created with the help of 3D printing is also possible from 2D structures, and this has prominent applications in engineering field. Despite the advantages of graphene in various applications, it also raises concerns

on toxicity. Many reports provide evidence for the potential toxicity of graphene and also for various graphene derivatives [24]. Rajni et al. investigated the nature of graphene and identified that it is an appropriate material for both transparent and non-transparent electrodes and can be suitable for double electrode designs for the super capacitors. It was observed from experiments that the in the applications such as flat panel displays, solar cells and in tough screens, graphene can be used for transparent electrodes [25]. In case of super capacitors, energy storage capacity is more important than the transparency. It was found that graphene has excellent potential in the above said application. The review article narrated the trending knowledge graphene and the patent base for its manufacturing. The investigation also included thorough study of US Patent Base to review the existing patents on transparent electrodes made of graphene for super capacitors and flat panel display devices. It was inferred that a large number of patents were on the application and fabrication of graphene super capacitors and flat panel display devices. More than 40 patents were covered in the article from 2015 to 2017 [26]. Rowley observed that as 2D material, graphene has paved way for significant interest due to its higher stability, excellent conductivity, and larger carrier mobility. In order to improve the energy storage performance the integration of graphene with the heterogeneous electrodes was found to be a highly effective method. In the study undertaken, the graphene-based heterogeneous electrodes were completely reviewed for its energy storage capacity. The study also illustrated the ball-milling, electro spinning, hydrothermal, and microwave-assisted approaches [27]. Brahim et al. investigated the innovative breakthroughs in graphene applications. It was observed that the fundamental research and vast industrial applications resulted in the larger and low-cost production of graphene for real world applications [28]. They insisted that graphene being a one-atom thick carbon crystal consist a set of unique physico-chemical properties. It was found to have extreme mechanical behavior, exceptional electrical, and also thermal conductivities. These attributed to the replacement of conventional materials with graphene for various applications. They discussed the probability of successful integration of graphene into a device for various applications in electrorheology, photovoltaic, shape memory, thermoelectricity, self-healing, and space missions [29]. Zhang et al. observed that graphene, an emerging carbon material, would be more of practical applications. The article highlighted research progress in graphene-based materials. Working principle of supercapacitors and research progress in synthesis and of graphene—based materials was studied. The graphene-based materials included for the study are carbon nanotubes, fullerenes, and graphene oxide. The study also included the applications of graphene-based materials for the design of advanced supercapacitors [30].

8 Challenges, Opportunities, and Future Perspectives

Graphene is the sheet of carbon of one atom thick, and the thinnest of all materials is considered as the prominent material of the 21st century materials science. It has greater number of practical applications in the manufacturing of sensors, terahertz

imaging, transistors, composites, membranes, batteries, energy storage devices, and thin coatings for LCD displays and solar cells. Above all graphene forms the basis of new breeds of computer chips, which are smaller and faster than those made of silicon. Researchers are now working to meet the challenges in graphene processing.

- One important aspect is to create large enough graphene sheets to pattern with conventional lithography.
- There are very few commercial suppliers of the thin layer of graphene, and it also requires manpower for the synthesis of the thin sheets.
- One cheaper method of production is depositing carbon atoms from a vapor onto an inert support. But in the process, the carbon atoms curl up around impurities, rather than forming as thin sheets.
- The chemistry part of graphene story has only just begun, and it has long way to move forward. However, chemists are working on to modify the structure to functionalize it effectively for various applications.
- Chemically modified graphene is still under research and not reached a level of sophistication yet.

Large scale application of graphene is still a challenging task. In case, flexible electronics require large graphene sheets with lesser defects. Current methods still face this challenge. Presently large-scale synthesis of graphene is dependent on graphene nano platelets produced by the modified hammers method. The process results in large graphene production, but the graphene produced is by non-friendly procedure owing to the nature of chemicals used. Standardization is associated with graphene production. For every run, the graphene produced finds variation in doping, quality, thickness, or even defects. Cost of production remains an empirical exercise and remains unsolved. The variation in graphene quality may occur even in the same lab. The variations in graphene properties may be observed with different vendors also. Hence there is a need for standardizing the production methods of various vendors and also the methods followed by different researchers. Graphene derivatives like graphene oxides, reduced graphene oxides, etc. have also exhibited values much lesser than what has been predicted for graphene material. From the above discussions, it can be inferred that making graphene industry-friendly, more efforts are required for synthesis, storage, and reduction in cost of production [31].

9 Conclusion

Graphene electrodes exhibit superior properties when used in microbial fuel cells. The unique properties of graphene such as transparency enhanced electrochemical property, high electrical, and thermal conductivity makes it the most appropriate material in various fields of application. Due to the superior chemical and physical properties of graphene, they have obtained significant attention in the design of microbial fuel cells for generation of electricity. The working mechanism of the MFC and production techniques were discussed in detail along with detailed study on its

applications. The merits and demerits of graphene-based electrodes and application of the same were also discussed. Reviewing the abundant works on graphene derived electrode materials, the chapter concludes with a perspective on the strategies and critical challenges in graphene derived electrode fabrication for further enhancement of MFC performance.

References

1. Guadarrama-Perez O, Gutierrez-Macias T, Garcia-Sanchez L, Guadarrama-Perez VH, Estrada-Arriaga EB (2019) Recent advances in constructed wetland-microbial fuel cells for simultaneous bioelectricity production and wastewater treatment: a review. Int J Energy Res 43:5106–5127
2. Fang C, Achal V (2019) The Potential of microbial fuel cells for remediation of heavy metals from soil and water—Review of application. Microorganisms 7(697):2–13
3. Do MH, Ngo HH, Guo WS, Liu Y, Chang SW, Nguyen DD, Nghiem LD, Ni BJ (2018) Challenges in the application of microbial fuel cells to wastewater treatment and energy production: a mini review. 639:910–920
4. Gude VG (2016) Wastewater treatment in microbial fuel cells e an overview. J Clean Prod 122:287–307
5. Ci S, Cai P, Wen Z, Li J (2015) Graphene-based electrode materials for microbial fuel cells. Sci China Mater 58(6):496–509
6. Slate AJ, Whitehead KA, Brownson DAC, Banks CE (2019) Microbial fuel cells: an overview of current technology. Renew Sustain Energy Rev 101:60–81
7. Mustakeem (2015) Electrode materials for microbial fuel cells: nanomaterial approach. Mater Renew Sustain Energy 4(22):2–11
8. Hou J, Liu Z, Zhang P (2013) A new method for fabrication of graphene/polyaniline nanocomplex modified microbial fuel cell anodes. J Power Resour 224:139–144
9. Zhao C, Wang Y, Shi F, Zhang J, Zhu JJ (2013) High bio current generation in Shewanella-inoculated microbial fuel cells using ionic liquid functionalized graphenenanosheets as an anode. Chem Commun 49:6668–6670
10. Min B, Cheng S, Logan BE (2005) Electricity generation using membrane and salt bridge microbial fuel cells. Water Res 39:1675–1686
11. Kim KY, Yang WL, Evans PJ, Logan BE (2016) Continuous treatment of high strength wastewaters using air-cathode microbial fuel cells. Bioresour Technol 221:96–101
12. Chaudhuri SK, Lovely DR (2003) Electricity generation by direct oxidation of glucose in mediator-less microbial fuel cells. Natl Biotechnol 21:1229–1232
13. Zhao C, Wang WJ, Sun D, Wang X, Zhang JR, Zhu JJ (2014) Nanostructured graphene/TiO_2 hybrids as high-performance anodes for microbial fuel cells. Chem Euro J 20:7091–7097
14. Fei Y, Wang C, Ma J (2016) Applications of graphene-modified electrodes in microbial fuel cells. Materials 9:2–27
15. Yang L, Wang S, Peng S, Jiang H, Zhang Y, Deng W, Tan Y, Xie MMQ (2015) Facile fabrication of graphene-containing foam as a high performance anode for microbial fuel cells. Chem Euro J 21:10634–10638
16. Yaqoob AA, Mohamad Ibrahim MN, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) Recent advances in anodes for microbial fuel cells: an overview, materials. 13:3–28
17. Youn DH, Jang J-W, Kim JY, Jang JS, Choi SH, Lee JS (2014) Fabrication of graphene-based electrode in less than a minute through hybrid microwave annealing. Sci Rep 4:1–8
18. Zhen Z, Zhu H (2018) "Structure and properties of graphene", graphene fabrication, characterizations, properties and applications, pp 1–12. ISBN 9780128126516

19. ElMekawy A, Hegab HM, Losic D (2016) Christopher P Saint and Deepak Pant. Applications of graphene in microbial fuel cells: the gap between promise and reality. Renew Sustain Energy Rev. https://doi.org/10.1016/j.rser.2016.10.044
20. Rahman MR, Moshiur Rashid MD, Mashrur Islam MD, Masum Akanda MD (2019) Electrical and chemical properties of graphene over composite materials: a technical review. Mater Sci Res India 16(2):142–163
21. Yuan H, He Z (2015) Graphene-modified electrodes for enhancing the performance of microbial fuel cells. R Soc Chem 7:7022–7029
22. Tavakoli MM, Azzellino G, Hempel M, Lu A-Y, Martin-Martinez FJ, Zhao J, Yeo J, Palacios T, Buehler MJ, Kong J (2020) Synergistic roll-to-roll transfer and doping of CVD-graphene using parylene for ambient-stable and ultra-lightweight photovoltaics. 30(31)
23. Su H, Hu YH (2020) Recent advances in graphene-based materials for fuel cell applications. Energy Sci Eng 9(7):958–983
24. Syama S, Mohanan PV (2018) Comprehensive application of graphene: emphasis on biomedical concerns. Nano-Micro Lett 1–31. ISSN 2311-6706
25. Garg R, Moussa M (2018) Graphene electrodes for applications in display devices, solar cells, and supercapacitors. Recent Patents Mater Sci 10(1):218–226
26. Wang N, Wang H, Yang G, Sun R, Wong C-P (2018) Graphene-based heterogeneous electrodes for energy storage. Graphene Deriv. https://doi.org/10.5772/intechopen.80068
27. Rowley-Neale SJ, Randviir EP, Dena AS, Banks CE (2018) An overview of recent applications of reduced graphene oxide as a basis of electroanalytical sensing platforms. Appl Mater Today 10:218–226
28. Nguyen BH, Nguyen VH (2016) Promising applications of graphene and graphene-based nanostructures. Adv Nat Sci: Nanosci Nanotechnol 7(2):023002
29. Aissa B, Memon NK, Ali A, Khraisheh MK (2015) Recent progress in the growth and applications of graphene as a smart material: a review. Front Mater, Article 58
30. Zhang LL, Zhou R, Zhao XS (2010) Graphene-based materials as supercapacitor electrodes. J Mater Chem (29)
31. Owuor PS, Khan A, Leon CL, Ozden S, Priestley R, Arnold C, Chopra N, Tiwary CS (2021) Roadblocks faced by graphene in replacing graphite in large-scale applications. Oxford Open Mater Sci 1(1)

Role of Microbial Community in Microbial Fuel Cells

Rozina Kakar, Ankita Rajendra Parab, Amirul-Al-Ashraf Abdullah, and Sundas Bahar Yaqoob

Abstract The catalytic activity of oxidation of organic molecules and their conversion into a biofilm is performed by microorganisms using electrical energy that is generated in the microbial fuel cells (MFCs). MFCs are considered to be a novel environmentally sustainable technology, to be used for bioremediation and energy production, since it generates energy from many organic substrates. MFCs technology can assist with have you metal removal and recovery. It has been reported that microbial strains may achieve enhanced power densities, compared to the power densities of the existing mixed community strains. This approach is only being employed on a laboratory scale due to a few constraints such as poor efficiency and low production rates. This chapter discusses the high-power generating bacteria found inside microorganism colonies, production of biofilm, the roles and mechanisms of various microorganisms in energy generation, removal of heavy metal, and electron transport in the fuel cell.

Keywords Microbial fuel cells · Heavy metals · Bacterial species · Biofilm

1 Introduction

Today, microbial fuel cells (MFCs), which are used to carry out environmentally sustainable processes such as bioremediation, are among the most fascinating electrochemical fuel cells. As illustrated in Fig. 1, the main components are the anode and cathode. It is a given fact that the great majority of microorganisms are used as biological catalysts, and therefore, the main principle of MFCs is the generation of energy using organic-inorganic matter which is abundantly found on the earth [1–3]. From many studies, it is clear that bacteria served as biocatalysts, capable of

R. Kakar · A. R. Parab · A.-A.-A. Abdullah
School of Biological Sciences, Universiti Sains Malaysia, 11800 Pulau Pinang, Malaysia

S. B. Yaqoob (✉)
Department of Zoology, Mirpur University of Science and Technology (MUST), Mirpur 10250, Azad Jammu and Kashmir, Pakistan
e-mail: sbahar.yaqoob@gmail.com

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_8

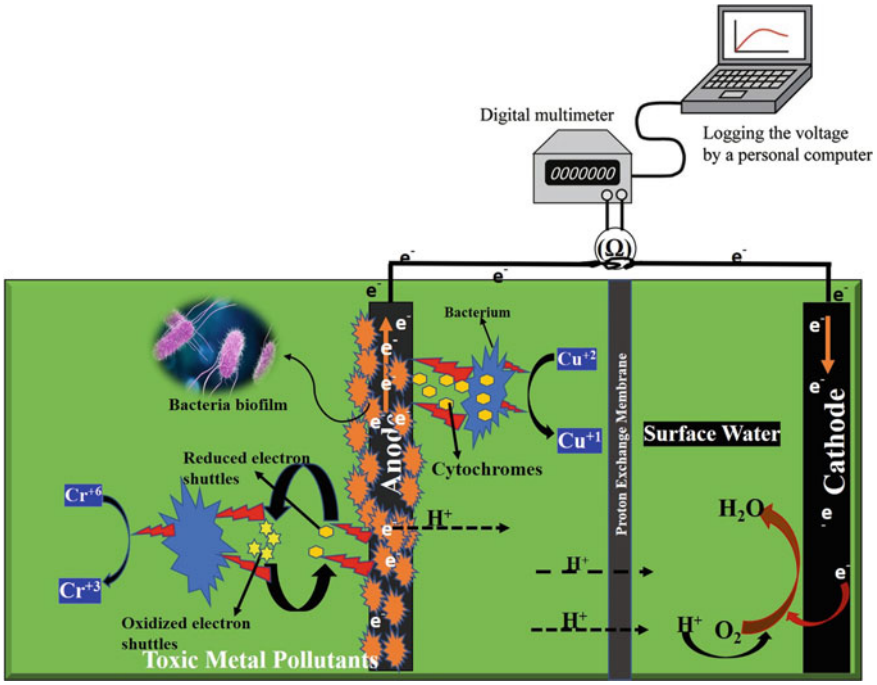

Fig. 1 The fundamentals of microbial fuel cells' setup and operation (MFCs). Adapted from reference [26] no permission needed

converting hydrocarbons and non-hydrocarbons to carbon dioxide. These bacteria can also generate electrons on the anode in an electrolyte which consists of reduced oxygen levels, to generate current and transmit electrons to the surface of the anode [4]. Electron carriers such as phenazines and flavins are fundamentally produced by the bacterial electron transfer on an anode. Electron carriers are also used in order to transmit electrons that are naturally present in the extracellular space [5]. Microbial nanowires may be used to create a conductive pili filament, which can carry electrons. In MFCs research, chemical mediators, for example, neutral red are used to move electrons from cell to electrode for energy generation [6]. The electrons carried at the anode react with oxygen in the cathode chamber and generate water molecules [7]. During the production of energy, the pollutant is reduced to an insoluble condition. MFCs are equally significant in the treatment of wastewater. Heavy metal contamination has always had an impact on the environment due to its extreme toxicity and density impact [8]. Therefore, heavy metals are particularly dangerous, even in little amounts. Along with this, they are hazardous to both marine life and human health [9]. Heavy metals are released into the air and waterbodies through chemical factories, dyeing plants, electroplating plants, and metal finishing industries. They're thick, non-biodegradable, and soluble in both surface and ground water [10]. It can be a major source of serious health risks for humans if consumed

in excess of the permissible concentration. Water pollution can also result from a number of factors. All the water supplies including ground and surface water are at risk due to a number of human activities such as industrial operations, agriculture, mining, and a variety of other activities [11]. These are considered to be the main culprit for the growing concentrations of heavy metals in water sources due to poor management and treatment of wastewater before releasing it into the waterbodies. Serious health issues are inevitable if a considerable portion is absorbed by humans. A heavy amount of absorption of chromium, for example, can result in major kidney problems, nerve tissue syndrome, skin irritation, skin ulceration, liver damage, and cardiovascular system issues [12]. Renal failure, bone deformities, and lung disease are majorly caused by excessive cadmium contamination. Copper and nickel, among other contaminants, can cause anemia, liver problems, renal failure, stomach pain, heart illness, and intestinal inflammation [13]. The most dangerous elements to human health are mercury and lead, which cause ailments such as kidney disease, lung disease, heart disease, the Hunter-Russel syndrome, brain damage, and skin disease [14]. Although arsenic is not a real metal, its properties fall between nonmetals and metals, making it a semi-metal. If arsenic levels in the body are too high, it can cause significant health problems [15]. The most common source of harmful arsenic is ground natural water, which has high amounts. Drinking arsenic-polluted water affects 137 million people, according to a case study conducted by the scientific community in 2007 [16]. As a result, the treatment of heavy metals is crucial. Heavy metals may be removed from wastewater in a variety of methods, according to scientists. There are a variety of pharmacological, biological, and physical therapy options, all of which are used in practice. The following techniques are now used: coagulation-flocculation, chemical precipitation, membrane filtration, electrochemical treatment technologies, and adsorption [17–20]. Many academics are eager to create a unique heavy metal treatment technique that is both cost-effective and ecofriendly. MFCs are a new technique for creating energy from wastewater treatment because of their low cost and long life. The reduction of oxygen at the cathode can be facilitated by the oxidation of organic elements on the anode [21]. When the redox potential of a molecule is higher than oxygen, then its reduction can occur at the cathode. In MFCs, ferricyanide, dye molecules, permanganate, persulfate, nitrate, and heavy metals have all been demonstrated to be sufficient electron acceptors [22]. Thermodynamically favorable conditions produced by the chemicals that are reduced allow the transfer of electrons from one rod to the other without using external energy. MFCs are a novel and interesting approach to generating energy at a low cost [23, 24]. The concept of generating energy through bacterial respiration has been discussed for over a century [25]. In addition, the current study assesses the metal remediation and mechanism of energy generation using MFCs. MFCs are made up of many different bacterial species, which are addressed in detail throughout this article.

2 Microorganism-Based Energy Production and Metal Remediation in MFCs

Numerous bacterial species can transport electrons via MFCs, which have a wide range of uses. Microalgae, proteobacteria phyla, yeast, fungus, iron-reducing bacteria, and acid bacteria are among the five categories of firmicutes that have exhibited energy generation in MFCs. The general species of bacteria which are capable of undergoing electron exchange with the respective electrodes include *Aeromonas hydrophila*, Shewanella sp., Geobacter sp., *Enterococcus gallinarum*, *Clostridium butyricum*, and *Rhodoferax ferrireducens* [27, 28]. Some of these bacterial species, such as *Geobacter* species, have electrical properties like biofilms, and conductive polymers can serve as supercapacitors [29]. Bacterial respiration produces electrons, which may be transported to electrodes and used to monitor electric current. Bacterial species generate a biofilm that allows electrons to move from anode to cathode. Carbohydrates are a typical organic substrate for bacterial metabolism and bioelectrogenesis in MFCs [30]. During the process of glycolysis, Acetyl coenzyme is produced from carbohydrate molecules which enter the tricarboxylic acid cycle (Kreb's cycle or citric acid cycle). One reduced flavin adenosine dinucleotide (FADH2) and three molecules of reduced nicotinamide adenosine dinucleotide (NADH) are produced as a byproduct of Kreb's cycle. This process generally occurs in the cytoplasm, where electron transporters produce NADH and FADH2, after which occurs the transmission of their electrons to the electron transport chain (ETC). These electrons travel through the ETCs following protein channels (NADH dehydrogenase, coenzyme Q, cytochromes, and ubiquinone) and eventually to the electron acceptor [31]. They are transported to the cathode electrode by pumping from the anode. This whole pattern generates roughly 34 adenosine triphosphate (ATP) molecules and H_2O from the carrier molecules, as shown in Fig. 2.

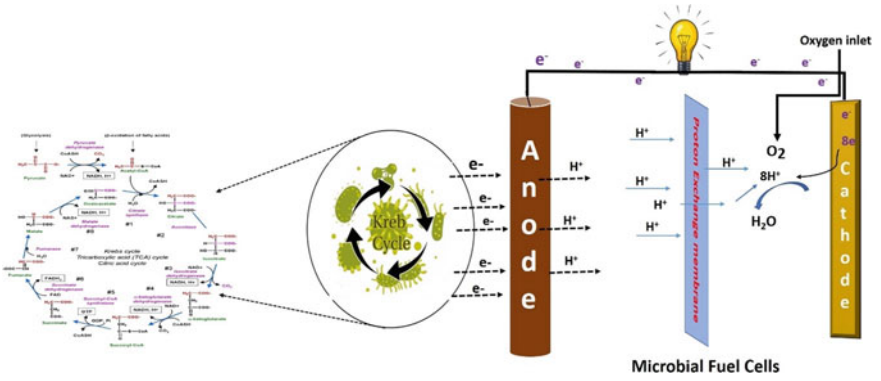

Fig. 2 A graphic depiction of bacterial metabolism showing the transfer of electrons from bacteria to the anode. Reproduced from reference [32] with Elsevier permission

Metal reduction during the production of energy is also considered a significant phenomenon. The absorption of electrons from electrodes, for heavy metal treatment through reduction, is carried out by special microorganisms under the group of Electrotrophs [33]. The discovery of electrotrophs has opened a new era of modern science. Several microbial consortia have shown electrotrophic characteristics until now [34, 35]. Gregory et al. [34] investigated the flow of electrons in the reverse way (from electrodes to microorganisms), which was followed up by Thrash and Coates [36]. In bacteria, various redox-active compounds act as electron transports. By providing electrons to bacteria, they can receive electrons from electrodes and enhance fermentation and inorganic substrate reduction. Such an electron potential is exhibited by some bacteria such as *Staphylococcus carnosus*, *Dechlorospirillum anomalous*, *Streptococcus mutans*, *Clostridium jungdahlii*, *Enterococcus faecalis*, *Acinetobacter calcoaceticus*, *Shigella flexneri*, *Kingella denitrificans*, and *Lactobacillus farciminis* [37, 38]. Bacteria generate a lowered electrode potential which facilitates the conversion of protons to hydrogen. The use of hydrogen gas is restricted, due to its explosive properties. To counterbalance the reduction of protons in hydrogen gas, it's either required to utilize a costly metal catalyst or to expend energy on the electrode. As a result, using electricity to power microorganisms is the most important approach for circumventing this restriction and reaching a high electron transfer rate. Hydrogen gas or other redox chemicals do not trigger the cells attached to the electrode, and only planktonic cells grow. While being removed from the products, the bacterial cell-electrode remains connected to them, enabling the cells connected with the electrode to be produced alongside the electrons [39]. *Geobacter* species were examined on electrodes as electron-accepting sp., after which Thrash and Coates [36] proposed the impact of microorganisms. Several Geobacter species function as electron acceptors, chlorinated solvents, reducing uranium (VI), nitrate, and fumarate. There are investigations that have demonstrated the ability of *Geobacter sp.* to promptly absorb electrons [40]. In *Geobacter. Sulfurreducens*, the sulfur reduction transport of electrons was distinct from the biofilm gene expression that received electrons from the electrode. The omcZ and pili genes are important since they generate electricity without having any influence on bacterial species' activity. Along with this, the gene deletion for cytochrome in order to generate electricity had no effect on electron transport on the electrode [41]. In order to reduce fumarate, *G. sulfurreducens* MR-1 also receives electrons. Riboflavin, which was generated as an electron transport mediator, in the presence of lactate, helps to reduce Cr(VI) via the Mtr pathway, which is similar to the electron transport outside of the cells [42]. The outer membrane of Acinetobacter ferroxidase, which reduces oxygen, has been seen to include Cytochrome c (Cyc2). The release of electron shuttles inside bacteria occurs when electrons are transferred to pyrroloquinoline quinone (*Acinetobacter calcoaceticus* and *Shewanella putrefaciens*). During Fe(II) oxidation and reduction, acidophilic Leptospirillum group II bacteria produce Cyt579 and Cyt572 as electron carriers [43]. In the case where the protons were used to reduce the number of electron acceptors in electron-receiving cells, the proton gradient was the only factor generated during this cross-membrane activity. The mechanisms of power storage in these cells are not well understood.

Since such biofilms which store current are thinner than current biofilms used for consumption, therefore, it implies that storing the current is better than its consumption [44]. Hence, the soluble U(VI) was converted to the insoluble U(IV) form by *G. sulfurreducens*, which got the electrons from the electrode. The electrode surface becomes coated with the insoluble U(IV) form once it has been adsorbed there. The SMFC electrodes were removed, and the immobilized U(IV) form was easily released [45]. Another hazardous, soluble form of Cr(VI) has been reduced by *G. Sulfurreducens* to a less poisonous, insoluble Cr(III). For the process of delivering electrons to these bacteria on the anode, Cr(VI) reduction on the cathode is completely dependent on the acetate oxidation and Cr(VI) reduction in the anode chamber. When bacteria are used for such processes, the organic materials have reduced from the state of being electron acceptors to electron donors. Methanobacterium palustre is an electron acceptor that can receive electrons and convert dehalogenated 2-chlorophenol to phenol, among other bacterial species [45]. Guan et al. [36] had used a power density of more than 540 mW/m^2 and discovered that Lactococcus, Enterobacter sp., and Macellibacteroides, after the pyrosequencing of 16S rRNA, can decrease the quantity of vanadium (V) by up to 93.6% [46]. Chlorobi, Armatimonadetes, Chloroflexi, Gammaproteobacteria, Spirochaetes, and Firmicutes were identified at quantities lying between 75 and 150 mg/L by Guan et al. [47]. These bacterial species can eliminate vanadium using the power output which is approximately around 420 mW/m^2 after almost 12 h of process. However, how electrons are absorbed by electrodes via molecular processes is yet unclear, which might be important for future study. Figure 1 also shows the metal reduction procedure in a methodical manner.

3 Electron Transfer Mechanisms Between Bacteria Cells and Electrodes

When generating bioenergy with MFCs technology, it is generally important for transporting electrons from the exoelectrogens respiration chain to the electrode. The process of microbes transferring electrons does not classify as a natural phenomenon. This mechanism has also yet to be explored [38]. As a result, numerous routes for electron transport from exoelectrogens to electrodes have been described. Generally, there are two methods for electron transport which are identified as indirect and direct electron transfer. Indirect electron transfer is where electron interaction is achieved through electron mediators and direct is where there is a direct interaction between the bacterial cell surface and the electrodes (Fig. 3).

Direct electron transport via the cell's outer membrane is considered to be an essential part of microorganisms' interaction during a fuel cell process. The electrogene produces biofilms at the anode surface using nanowires that conduct electricity (mainly, flagella, and pili) [39]. Direct contact allows the electron to pass between the cytochrome and nanowires. Transmembrane electron transport via proteins, as

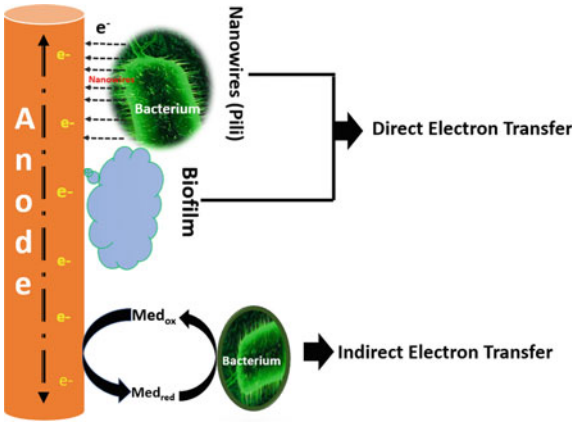

Fig. 3 Exoelectrogens' electron transport mechanism to the anode. Adapted from reference [26] no permission needed

well as restricted diffusional electron mediators, is implemented as well. The electron acceptor electrode is not in direct contact with the cell. Exoelectrogens can access the membrane since the nanowires are connected to cytochromes adhering to it. Transport proteins are critically important since they are responsible to directly transfer electrons to the anode from the cytoplasm. Primarily an alternative for direct electron transfer is to generate an effective current in MFCs. There is one major disadvantage of direct electron transfer. The rate of electron transfer is very low because the active regions of the transport proteins are hidden inside proteins [40]. Electrochemically active bacteria, such as Geobacter and Shewanella, are among only a few species, that are known to use bacterial nanowires to transport electrons away from the cell [41]. Lower soluble molecular-based mediators are used to carry out electron transport. The requirement of having intimate contact between electron acceptor and bacterial cells is diminished when indirect electron transfer occurs. The electron shuttles infiltrated bacterial cells and collected electrons from exoelectrogens metabolic activities, which were subsequently supplied to the anode electrode. In order for the MFCs to work, it was assumed that the presence of electron mediators was an essential component. They can be created with exoelectrogens or applied to an anode externally. Self-mediator syntheses including pyocyanin, phenazine, and others have been identified in several types of bacteria. Because of the potential difference, redox proteins and mediators will have a significant impact on electron transfer efficiency [48]. A number of chemical combinations have been tried to improve electron transference efficiency, including humic acid, neutral red, anthracenedione, riboflavin, methylene blue, and thionine [49, 50]. It is not recommended to use exogenous mediators, because they frequently result in low current densities while also becoming expensive and damaging to microorganisms, allowing poor efficiency over extended periods, and making the technology difficult to market.

Furthermore, adding exogenous mediators daily is both industrially and ecologically unfeasible.

4 Electrode Biofilm

A microbial city is a term used to describe a biofilm. Lipids, Carbohydrates, proteins, and other substances are found in the polymeric matrix. It's generally because of the bacteria that reside on its surface; it's the best habitat for them to thrive in, therefore, they create a biofilm. The creation of electroactive biofilms can provide efficient energy. The production of biofilms may be tracked by a variety of routes, which are most likely dependent on the microorganisms employed in MFCs, as well as the operating parameters, electrode material, and MFCs substrates. According to several recent research, the physical and morphological characteristics of the electrode might influence biofilm development [51, 52]. Recent studies have confirmed the inability of bacteria to form biofilms on electrodes. This can also be related to their inability to produce significant current densities in fuel cells, according to recent research. Biofilms can be formed by many bacteria and compared to such bacteria; the anode bacteria can produce greater current densities on thick biofilms. *Thermincola ferriacetica*, a Gram-positive bacteria, can produce a constant current density of 7–8 A/m^2 while building thick biofilms (38 m) [53]. Meanwhile, lower current densities may be observed for *Thermincola potens*, along with producing monolayer biofilms [54]. Microbe adhesion to the surface and migration toward the surface, growth of microcolonies, and biofilm maturation are some of the mechanisms that might trigger the process of formation of biofilm formation in the fuel cells on the electrode [49]. Biofilms are formed when bacteria synthesize nucleic acids, sugars (polysaccharides), proteins, adhesion molecules (adhesins), and other molecules that interact and coat one other [50]. Electroactive biofilms can inhale via terminal electrons onto electrode surfaces during their metabolism. Redox-active molecules such as Flavins have the capacity to lower the externally occurring cellular electron transfer in Shewanella sp. during biofilm formation [55]. During the formation of biofilm in *Pseudomonas aeruginosa*, rigorous flagellar motion transfers bacteria on the surface. A 'mushroom-shaped' biofilm can be formed via a maturation process that necessitates signaling pathways with pili (type IV), which gives rise to microcolonies and aggregation of the cells [56]. Quorum sensing (QS) is a mechanism in the bacterial population that allows cooperation and interaction of collective behavior in the bacterial colonies. QS controls the outflow of biofilm-related characteristics to aid biofilm development in *P. aeruginosa* and other bacteria. The power density is observed to be higher in biofilms with a mixed culture than the pure culture. When injected into MFC, the mixed or varied culture had a power efficiency of about 20% greater than the pure culture [57]. Non-exoelectrogens' involvement and producing power, on the other hand, are unknown. Direct contact is established by bacterial cells with the anode electrode surface, which facilitates the bypassing of c-type cytochromes and

allows electrons to flow straight to the anode. At the cathode, the use of microorganisms to catalyze oxygen reduces the interest in cathodic biofilm. In contrast to anode biofilms, the age impact of cathode biofilms appears to diminish as the width of the biofilm grows [58].

5 The Importance of Bacteria in MFCs

Many microorganisms have been investigated for energy production, bioremediation, and a variety of other fundamental uses. The substrate for the MFCs is derived from a variety of sources, including wastewaters (chocolate industry water, brewery wastewater, recycling paper wastewater, paper recycling wastewater, swine wastewater, and brewery wastewater), as well as a variety of nutrients (lactate, glucose, acetate, sucrose, starch, xylose, and ethanol) [59]. Power can be generated by only a small percentage of the microorganisms found in the fuel cells. Their anodic chambers utilize exoelectrogens from cyanobacteria, Gram-positive/negative bacteria, yeast, algae, and fungus [60]. Different bacteria that produce enough energy can oxidize the complex biological substance into its constituents (Table 1). Specific exoelectrogens, on the other hand, may oxidize specific substrates in order to produce energy. Furthermore, every exoelectrogens has various oxidation or reduction pathways as well as genes, proteins, or enzymes, which depend on the substrate type [61]. The performance of MFCs is, thus, determined by the choice of efficient bacterial consortia and the desired substrate. For example, when aerobic/anaerobic slush and glucose is added as an inoculant, for three months in MFCs, they were able to generate and convert power [62]. Organic compounds, such as carbohydrates, proteins, and fats, are utilized in MFCs to create energy through redox anode processes because of their ability to donate electrons. Eventually, various organic compounds ultimately carry out acetyl Co-A dispensing activities and contribute to Kreb's cycle. Reduced NADH, FADH2, and CO_2 are liberated as by-products in one cycle [63]. Glycolysis and the Krebs cycle are metabolic processes found in the cytoplasm of both eukaryotes (yeast) and prokaryotes (bacteria). FADH2 and NADH are carriers of electrons which then transport them to the ETC in order to produce the energy molecule, ATP. The respiratory complex is contained in the cell membrane and is a place where the respiratory processes of bacteria take place. It generally comprises of the outer and inner cell membrane, and the space in between them (periplasm) [64]. All of the proteins or enzymes necessary for electron transport are found in yeast in the mitochondrial membrane (MFC base). ETC generally consists of cytochromes, NADH dehydrogenase, ubiquinone, and coenzyme Q. It is highly likely to observe species differences among these intermediate proteins. In the anode, the reduced protons are pumped out of the cells and then delivered to the cathode by PEM, and electrons are transported to the last electron acceptor [61]. Before the concept of bacterial electron transport facilitators, chemical intermediates were utilized for the catalysis process of electron transport from the bacteria to the anode. When they react with the constituents of ETC, they lose and transfer electrons to the anode. Bacterial

Table 1 Remediation of heavy metals: summary, efficiency, and energy generation through MFCs

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Anaerobic sludge	V	240	30	Carbon fiber felt	Carbon fiber felt	100 mg/L	67.9 ± 3.1	970.2 ± 60.5 mW/m^2	Lwalaba et al. [69]
Mixed microbial culture	Cr	26	25	Graphite plates	Graphite plates	26 mg/L	97	–	Lwalaba et al. [69]
Shewanella oneidensis MR-1	Cr	192	30	Graphite felt	Graphite rod	200 mg/L	67	32.5 mW/m^2	Thrash and Coates [36]
Shewanella genus	Au	–	25	Pt-graphite	Pt-graphite	200 ppm Au with 1,000 ppm standard solutions of HAuCl4	60	–	Jiang et al. [70]
Actinobacteria, *ß-Proteobacteria,*	Cr	144 and 192	35	Graphite felts	Graphite felts	5 mg/L 25 mg/L	5 mg/L With 93, 25 mg/L With 61	–	Huang et al. [71]
Sludge mixture	Ag	8	25	Carbon brush	Carbon cloth	50–200 ppm	99.91	4.25 W/m^2	Li et al. [72]
Anaerobic sludge	Cr	240	30	Carbon fiber felt	Carbon fiber felt	100 mg/L	75.4 ± 1.9	970.2 ± 60.5 mW/m^2	Lwalaba et al. [69]
Indigenous bacteria from Cr(VI)	Cr	173	22–26	Graphite plate	Graphite granular	39.2 mg/L	–	6.9 W/m^3	Ryu et al. [73]
Mixed microbial culture	Cu	–	25	Graphite felt	Graphite felt	10–200 mg/L	> 99	0.319 W/m^2	Huang et al. [74]

(continued)

Table 1 (continued)

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Oil sands tailings affected water	Hg	800	21 ± 0	Carbon cloth	Carbon cloth with Pt coating	581 ± 26 Se, 226.4 ± 4.7 Ba, 152.8 ± 16.8 Mo, 35.8 ± 13 Pb	97.8 Se, 96.8Ba, 77. Mo, 32.5 Pb	392 ± 15 mW/m^2	Wang et al. [75]
Mixed microbial culture	Cr	150	25	Graphite plates	Graphite plates	200 mg/L	100	0.150 W/m^2	Huang et al. [74]
Shewanella decolorationis S12, K. pneumonia	Cr	3.5	30	Carbon felt	Carbon felt	10 mg/L	99.9	52.1 mW/m^2	Zhang et al. [76]
Mixed microbial culture	Cu	480	27	Graphite felt	Graphite felt	600 mg/L	92		Huang et al. [74]
Anaerobic granular sludge	V	72	35	Carbon fiber felt	Carbon fiber felt	25 mL	87.9	578.3 mW/m^2	Vickers [77]
Anaerobic sludge	Cr	26	22	Unpolished graphite plate	Natural rutile-coated polished graphite	26 mg/L	97	–	Choi and Cui [78]
Mixed microbial culture	Cu	264	25	Graphite plate	Graphite plate	200 mg/L	>96	339 mW/m^3	Huang et al. [74]
Domestic wastewater	Cr	150	25	Graphite plates	Graphite plates	100 mg/L	100	150 mW/m^2	Nancharaiah et al. [79]
Sewage sludge	Cd, Zn	–	32	Carbon cloth (no wet proofing)	carbon cloth (30% wet proofing)	200 mM Cd; 400 mM Zn	Cd 90, Zn 97	3.6 W/m^2	Abourached et al. [80]

(continued)

Table 1 (continued)

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Anaerobic sludge	Cu	144	35	Graphite felt	Graphite plate	500 mg/L	70	314 mW/m^3	Zhang et al. [81]
Mixed microbial culture	Cr	48	25	Carbon cloth	Carbon cloth	100 mg/L	99	0.767 W/m^2	Huang et al. [74]
Dysgonomonas and Klebsiella	V	168	22 ± 2	Carbon fiber felt	Carbon fiber felt	200 mg/L	60.7	529 ± 12 mW /m^2	Tandukar et al. [82]
Algae biomass	Cr	96	–	Activated charcoal	Activated charcoal	200 mL	98	207 mW/m^2	Burscher et al. [83]
Tetrachloroaurate wastewater	Au	12	25	Carbon brush	Carbon cloth	2,000 ppm	99.89	6.58 W/m^2	Wu and Chen [84]
Anaerobic digestion sludge	Cr	16	–	Carbon felt	Carbon felt	50 mg/L	98	343 mW/m^2	Ya-Li et al. [85]
Mixed microbial culture	Cu	144	–	Graphite plate	Graphite foil	1 mg/L	99.8	0.80 W/m^2	Huang et al. [74]
Mixed microbial culture	Ag	26	–	Graphite plate	Graphite felt	200 mg/L	95	0.109 W/m^2	Huang et al. [74]
Anaerobic cultures mixed with Cr(VI)	Cr	1080	22–24	Graphite plate	Graphite plate	80 mg/L	60	55.5 mW/ m^2	Singhvi and Chhabra [86]
Klebsiella sp. MC-1	Cr	75	25	Carbon cloth	Carbon cloth	50 mg/L	99.1	412 mW/m^2	Li et al. [87]
Anaerobic sludge bed	Pt	24	25	Graphite plate	Graphite plate	16.88 mg/L	90	844.0 mW/ m^2	Huang et al. [74]

(continued)

Table 1 (continued)

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Anaerobic sludge	V	72	25	Carbon fiber felt	Carbon fiber felt	500 mg/L	25	0.572 W/m^2	Huang et al. [74]
Anaerobic sludge	Cu	20	35	Graphite plate	Graphite felt	200 mg/L	> 99	314 mW/m^3	Huang et al. [74]
Anaerobic sludge with Copper	Cu	144	35	Graphite felt	Graphite plate	500 mg/L	70	314 mW/m^3	Zhang et al. [81]
Anaerobic sludge	Hg	10	30	Graphite felt	Carbon paper	100 mg/L	98.22–99.54	433.1 mW/m^2	Gai et al. [88]
Mixed microbial culture	Cd	168	25	Graphite felt	Graphite felt	50 mg/ml	60	700–750 mW/m^2	Modin et al. [89]
Lithium cobalt oxide Solution	Co	–	35	Graphite felt	Graphite felt	200 mg/L	62.5 ± 1.8	298 ± 31 mW/m^3	Choi and Hu [90]
Sediment sample	Cr, Cu	2160	37	Graphite felt	Graphite felt	250 mg/L	96	400–450 mW/m^2	Wang et al. [91]
Mixed microbial culture	Se	48	25	Carbon cloth	Carbon cloth	75 mg/L	99	2.90 W/m^2	Huang et al. [74]
Geobacter and *Pseudomonas*	Cu	–	25	Carbon brush	Reduced Graphene oxide	12 mg/L	98	0.95 W /m^2	Liu et al. [92]
Anaerobic sludge	Cr	–	25	Graphite brushes	Graphite granules	10 mg/L	94	6.4 W/m^3	Huang et al. [93]
Anaerobic sludge	TI	72	22 ± 2	Carbon felt	Plain carbon paper	100 µg/L	67	457.8 ± 15.2 mWm^{-2}	Abbas et al. [94]
Mixed microbial culture	Hg	360	25	Graphite felt	Graphite felt	25 mg/ml	55	800 mW/m^2	Modin et al. [89]

(continued)

Table 1 (continued)

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Activated sludge	Cu	672	35	Graphite felt	Graphite plate	100 mg/L	96	140 mW/m^2	Huang et al. [93]
Mixed microbial culture	Ag	8	–	Carbon brush	Carbon cloth	200 mg/L	99	4.25 W/m^2	Huang et al. [74]
Dilute synthetic sample	Cd, Zn	1344	25	Carbon felt	Carbon felt	7.4 mg/L Cd^{2+} 19.5 mg/L Zn^{2+}	Cd 82, Zn 89	–	Gai et al. [88]
Anerobic pure culture	Cr, Cd	24	30	Carbon rod	Graphite felt	Cr(VI) 385 μM, Cd (II) 179 μM	73 for Cr, 61 for Cd	14.2 mW/m^2	Tao et al. [95]
Anaerobic sludge	Cu	20	35	Graphite plate	Graphite plate	6412.5 ± 26.7 mg Cu^{2+}/L	>99	339 mW/m^3	Huang et al. [74]
Anerobic pure culture	V	–	30	Carbon fiber felt	Carbon fiber felt	–	68	970 mW/m^2	Huang et al. [93]
Primary clarifier effluent	Cr	2	22 ± 3	Graphite brushes	Graphite granules	20 mg/L	76	970 mW/m^2	Huang et al. [93]
Mixed microbial culture	Au	–	–	Carbon brush	Carbon cloth	200 mg/L	99.8	6.58 W/m^2	Huang et al. [74]
Activated sludge	Zn	–	25	Carbon cloth	Carbon cloth	–	97	3600 mW/m^2	Huang et al. [93]
Mixed microbial culture	Pb	2592	25	Graphite granules	Carbon felt	900 mg/L	44.1	3.6 mW/m^2	Abbas et al. [94]
Contaminated soil	Cd	3432	25	Graphite granules	Carbon felt	100 mg/L	31	7.5 mW/m^2	Kumareet al. [96]
Anaerobic sludge	Ag	21	26	Carbon cloth	Graphite felt	1000 mg/L	99	0.3 W/m^2	Huang et al. [74]

(continued)

Table 1 (continued)

Incubation source	Target metals	Operating Time (h)	Temp (°C)	Electrodes	Initial Conc	Removal efficiency (%)	Power density	pH	References
Dilute synthetic sample	Cu, Pb	864	25	Carbon felt	Carbon felt	1.1 mg/L Cu^{2+}, 2.5 mg/L Pb^{2+}	Pb 92, Cu 99	17.1–25.2 mW/m^2	Luo et al. [97]
Mixed microbial culture	Cr	–	30	Carbon brush	Carbon cloth	100 mg/L	99	419 mW/m^2	Huang et al. [93]
Mixed microbial culture	Co	48	30	Graphite felt	Graphite felt	1000 mg/L	99.15	–	Huang et al. [74]
Anaerobic sludge	Ni	24	30 ± 1	Graphite felt	Graphite plate	26.4 mg/L	95	0.68–0.7 mW/m^2	Habibul et al. [98]
Mixed microbial culture	Ni	720	25	Graphite felt	Graphite felt	32.9 g/180 ml	–	150–200 m W/m^2	Modin et al. [89]
Anaerobic sludge bed	Cu	5	35 ± 1	Carbon brush	Carbon cloth	12.5 m/Lg	98.3	0.2 W/m^3	Wang et al. [99]

metabolism switches from phosphorylation to fermentation, when they have a potential anode [65]. Bacteria select fermentation metabolism when electron acceptors are very few. When there are enough electron acceptors and the anode potential is low, bacteria convert to oxidative metabolism as electrons collect on them. Geobacter sp., which are anaerobic, oxidizes around 33.33% of electrons required for electricity generation in the fuel cell during the fermentation processes. Clostridium sp. and Enterococcus sp. are among the several bacteria which are able to produce fermentation products in addition to the production of energy after adding them to the fuel cells anaerobically [66]. The most potent exoelectrogens found in MFC are *Geobacter* sp. and *Clostridium* sp. They are considered to be the most efficient source of hydrogen in biofilms. In MFCs, they possess greater power densities than pure cultures of mixed microorganisms. This is because they are capable of performing a network of metabolic activities between the bacteria. Although theoretically true, this must be clearly defined and experimentally proven [67]. The capacity of the anode is crucial in determining metabolic activities in bacteria. When the anode potential is negative, it gives electrons to the bacteria, causing them to form additional reduced complexes. Consequentially, bacteria will consume lower energy, and the recovery of the spent energy in the fuel cell is higher, resulting in higher power generation. Clearly, the colonies of microorganisms consisting of bacteria, capable of reducing sulfates, produced higher power density at negative anode potentials of 45 mA/m^2 at 0.6 V versus 15 mA/m^2 at 0.2 V [68]. MFCs efficiency has also been found to be improved by adjusting the cathode potential. According to the study, with a fixed cathode potential of −300 V, reducing the MFC for Cr(VI) raised the highest power density from 4.1 to 6.4 W/m^3 (control, variable potential). This also managed to reduce the initiation duration by 7 days creating a new time period of 19 days.

6 Anodic Bacterial Species

The Geobacteraceae bacterium family is the most researched and effective exoelectrogens in MFC technology. To generate energy, *G. sulfurreducens*, α-proteobacterium, may reduce acetate with nearly 100% electron retention. The species effectively generated a current density of more than 3000 mA/m^2 in an MFC using metal electrodes. Acetate and fumarate compounds were used as electron acceptor and donor, respectively [100]. Pure cultures of *Geobacter metalloproteins* are able to provide 40 mW/m^2 power output when wastewater is used as an inoculum in MFCs. Shewanella sp., proteobacteria, on the other hand, may reduce manganese and iron levels by utilizing them as electron acceptors [101]. Lactate *Shewanella oneidensis* DSP10 and ferricyanide were utilized and employed as anolyte and catholyte, respectively, resulting in a power density of 3000 mW/m^2 in a small MFCs [102]. It employs $CaCl_2$ as an anolyte to achieve the greatest power density of 4.92 W/m^3 in an MFC with a single compartment [103]. Some pure culture MFCs are considered to be exceptionally high yielding when compared to mixed cultures. Bacteria such as *Rhodopseudomonas palustris*, a photosynthetically active,

purple non-sulfur bacteria, utilize thiophosphate, yeast extract, and volatile acids at a power density of 2720 mW/m^2 in such fuel cells. Acetate gives the thermophilic Gram-positive metal-reducing bacteria *Thermincola ferriacetica* the highest power density of 12 A/m^2. Proteobacteria produce a power density of 4310 mW/m^2. Glucose is utilized as an electron acceptor and donor when graphite electrodes are used in fuel cells containing *Pseudomonas aeruginosa* and *Desulfovibrio desulfuricans* [66]. A bacteria which is capable of reducing sulfates achieved the greatest power density of 233 mA/m^2 using graphite electrodes treated on the surface in MFC, demonstrating a 50% increase over untreated electrodes [104]. *Escherichia Coli*, a Gram-negative bacterium, provided 1300 mW/m^2 of energy efficiency at 3390 mA/m^2 using MFCs. In an MFC containing an exposed cathode and graphite which is also non-catalyzed, along with synthetic wastewater, *Saccharomyces cerevisiae* generates 282.83 mA/m^2 power density [105]. Several yeast *Hansenula anomala* obtained 2.9 W/m^3 current density using a catholyte, ferricyanide, and Platinum as the electrode [68]. *Candida melibiosica* was used in MFCs to achieve 720 mW/m^2 current output using nickel nanostructures, on an altered carbon supplied electrode [106]. A few microbes that aren't often employed in MFCs have also demonstrated the potential to generate current. Along with this, a few new exoelectrogens have just been identified. The 16S rRNA gene sequence analysis identified a novel exoelectrogen, *Geobacter anodireducens*, which has a similarity of more than 95% to *Geobacter sulfurreducens.* However, it is unable to decrease the electron acceptor, fumarate [107]. Another new strain 575, Ochrobactrum sp., was recently identified from the anode compartment of a xylose base MFC and produced the highest power density of 2625 mW/m^3. The data also revealed that Ochrobactrum sp. digested xylose very uniquely, by using 'succinate oxidation respiratory chain' instead of the usual NADH oxidation respiratory chain. In another MFC, *Kebsiella pneumonia* (Gram-negative), lactose fermenting, produced 199.2 mA/m^2 current density and 426.2 mV maximum voltage output [108]. *Lysinibacillus spherics* (Gram-positive) produced the highest current density of about 270 mA/m^2 and a power density of 85 mW/m^2 in MFCs with graphite as an electrode [106]. Citrobacter sp. SX-1, on the other hand, may employ a variety of basic compounds in MFCs, including carbohydrates, glycerol, and acetate, although citrate has a maximum current density of 205 mA/m^2 [109]. Other than bacteria, microorganisms such as algae and yeast have been utilized previously as bioactive-anode or substrate supporting the anode in MFCs. Scenedesmus, a green algae, as a powder substrate and *Chlorella vulgaris* as a bioactive-cathode in MFCs produced a total power density of 1926 mW/m^2 [110]. Another study employed an arthrosporic base as a carbon source as well as a substrate for metabolism and development. Palustris had the highest power density of 10.4 mW/m^3 in volume in micro-MFCs when compared to the other substrates employed in the study [111]. Cyanobacteria or blue-green algae produced a maximum power density of 114 mW/m^2 in the MFC at a current density of 0.55 mA/m^2 [112]. In microalgae-assisted MFCs, exoelectrogenic agents like *G. sulfurreducens* may benefit from intermediate compounds created by algal degradation, such as acetate and lactate.

7 Bacterial Cathodic Species

Geobacter sp. is also used as biocathodes in MFCs to receive electrons from cathodic electrodes. *G. sulfurreducens* is capable of actively reducing fumarate to succinate in a fuel cell containing electrodes made up of stainless steel material, yielding a current density of 20.5 A/m^2, whereas *G. metallireducens* may reduce nitrate to nitrite [113]. In hybrid air-cathode MFCs, with a maximum current density of 32.5 mA/m^2, the Cr(VI) reduction rate is substantially improved by using *Shewanella oneidensis* MR-1, which acts as a biocatalyst, and also lactic acid acts as the electron donor. The study uses external membrane-bound cytochromes to report the function of Riboflavin in the transport of electrons. *Shewanella putrefaciens* and Acinetobacter calcoaceticus were found to be capable of rapidly reducing oxygen in water [114]. *Acidithiobacillus ferrooxidans*, an acidophile microbe found in MFCs, may feed as a biocathode with current densities up to 5 A/m2 and oxygen reduction at low pH. The electrochemical reduction of oxygen on acetate oxidation catalysis yields the highest current density [115]. As demonstrated by cyclic voltammetry, *Micrococcus luteus* and other Gram-positive and Gram-negative bacterial species such as Staphylococcus sp. and *Lactobacillus farciminis* and *Escherichia coli*, *Pseudomonas fluorescens*, and Acinetobacter sp., respectively, may help to promote the electrochemical reduction of oxygen on the carbon electrode. Stainless steel electrodes, dipped and coated in seawater, developed aerobic biofilms at varied set potentials, demonstrating effective catalysis of reducting the oxygen and producing current densities up to 460 mA/m^2 [116]. The highest power density of an MFC containing acetic acid, with *Chlorella vulgaris* as a biocathode, was 1926 mW/m^2. During its development, *C. vulgaris* used CO_2 from the anode as a carbon source. *C. vulgaris* did not grow in such MFCs when CO_2 was not available on the anode, according to the study. While *C. vulgaris* were undergoing immobilization, the MFCs functioned remarkably well in the cathode compartment, achieving a power density of almost 2485.35 mW/m^3 and a current density of about 7.9 A/m^3. Using the *C. vulgaris* white-rot fungus, *Coriolus versicolor* secretes laccase which reduces oxygen at the cathode. Inoculating this in the cathode compartment to catalyze the cathode reaction, the MFC obtained a total power density of 320 mW/m^3 [117].

8 Heavy Metals Removal Through MFCs

8.1 Chromium

It can be found in two oxidation states in the earth's crust, namely Cr(III) and Cr(IV). In terms of metal industry pollutants, the Cr(VI) state is considered harmful, and it contributes to the carcinogenic sources in the environment. Because of its toxicity, removing it from the environment is a significant challenge [118, 119]. As per the findings, graphite paste electrodes are used to eliminate chromium for the first time.

The investigation reveals noteworthy data, for example, a power density of 150 mW/m^2 and a lowered rate of 0.67 $g/m^3/h$ at a concentration of 200 mg Cr(VI). Furthermore, rather than utilizing the costly membrane, studies revealed that the salt bridge can reduce Cr(VI) more efficiently, with power density ranging from 92.65 W/m^2 for 5 mg/L of Cr(VI) to 75.08 W/m^2, for about 80% of 10 mg/L of Cr(VI) [120]. Prior study has demonstrated that in MFCs, an imbalance of pH between both the anionic and cationic compartments makes the system unstable and reduces the capacity to generate bioelectricity [120]. The usage of bipolar membranes improves performance and increases bioelectricity generation while assessing the problem. It also improves the potency of the Cr removal process (VI). Due to the passage of electrons and PEM, the pH in the entire apparatus was reduced. It not only cuts costs, but also expands the range of MFC reductions. In previous research, the efficient carbon nanofibers (CNF) electrode, coated with other elemental nanoparticles such as alumina or nickel, was successfully used in MFCs without any mediators [120]. In a prior work, Cr(VI) was removed at a specific capacity of 93% cathodic dipole action. A study has addressed Fe(III) as a mediator in MFCs to enhance Cr reduction (VI) [120]. Fe(III) has been discovered to be a cause of improved cathodic columbic efficiency as well as a reduction in Cr rate (VI). The electrodes utilized for efficient Cr removal, which are entirely made up of carbon compounds, have been proven. Moreover, due to the electrochemical reduction of Cr, carbon cloth has the most effective operation in these three electrodes (VI).

8.2 Vanadium

It is formed in large quantities, with an annual output of around 38,000 tons. For its unique qualities, such as shock resistance and steel vibration, known as steel addictive, Vanadium is also thought to be useful in the treatment of a variety of human diseases. In the anode chamber, various kinds of microorganisms known as *Rhodoferax ferrierducens* are used to reduce Vanadium (V). The current range was increased to 0.06 mA by adding 300 mg/L of $NaVO^3$ to the anode chamber [120]. The decrease of V was influenced by a number of variables, including pH, temperature, and stirring speed. Kilicarslan et al. [121] were the first to develop the advantageous method of using two distinct electron acceptors in the cathodic chamber. Not only is V reduced, but Cr(VI) is reduced as well. In this investigation, with only one electron acceptor, the power output demonstrates remarkable effectiveness. Interestingly, V and Cr(VI) had reduction efficiencies of 67.9 and 75.4%, significantly, demonstrating the study's high-power output demand.

8.3 Copper

When it comes to supply and demand, this element is a matter of contention across the world. The recovery and extraction are critical for researchers since it is produced from industrial and radioactive wastes [122]. It is recognized to be a hazardous substance for both humans and the environment. Its elimination is more important than its recovery stage due to its toxicity. Birloaga et al. [115] MFCs with bipolar membranes improved copper removal efficiency to 99.8% while achieving the highest power output of 0.43 W/m^2. Anaerobic conditions in the cathode compartments are used for the whole apparatus. Cu removal in MFC anodic chambers using sulfate-reducing bacteria has also been reported in the literature. This metal promotes biological processes by increasing MFC performance at lower concentrations of metal up to 20 mg/L [123]. It was accomplished by making four changes to lower internal resistance. The anode and cathode compartment separation was lowered to 0.5 cm. The next step is to reduce the internal resistance by using an anion exchange film and to use the copper plate as a cathode rather than graphite. The last step would be to use the carbon felt as the anode. This would help to increase the surface area [124].

8.4 Silver

It's one of the best valuable components found in a variety of industrial wastes. Having distinctive properties, such as malleability, firm strength, light reflexiveness, ductility, and high conductivity make it increasingly in demand in the fields of decorations, photography, and electronics [125]. This element's main disadvantage is that it has fewer natural resources and is less readily available. That is why, for economic and environmental reasons, experts have retrieved this element from industrial effluents. Adsorption, chemical precipitation, bio reduction, and bio absorption were described in the literature as techniques for removing Ag from wastewater [88]. After 8 h of work, the cost-effective MFC removed 99.91–98.26% of the silver, according to one research. It has a power density of 4.25 W/m^2 at starting concentrations between 50 and 200 ppm [126]. In cathodic chamber reduction, acetate is used as an electron donor, 95% of the silver was removed found in another research [127]. In the presence of ammonia, silver is removed, generating more than 3 J of energy and yielding approximately 1.6 g of silver in its pure form on the cathode. Anode compartments were decontaminated with 1 g of COD (83%) [69].

8.5 Cobalt

Cobalt is an important biological element that functions as an enzyme cofactor in living organisms, which is why it is regarded as a helpful cofactor. It's also hazardous

in terms of the body's and ecosystem's overconsumption. In humans, it can cause significant illnesses including asthma, lung cancer, contact dermatitis, and pneumonia. Because of its high potential (1.61 V), Co(III) is an excellent terminal electron acceptor in MFCs, according to the literature [69]. Adding Cu(II) to MFCs also increased cobalt leaching and acid utilization efficiency by 308% and 171%, respectively [128]. Table 1 summarizes the metal removal by MFCs.

9 Future Recommendations

Unfortunately for MFC technology, the technique's researched applications are currently restricted to the laboratory. To put it another way, the technology has not yet been commercialized. Only *Shewanella sp.* and *Geobacter sp.* have well-understood electron transfer pathways from exoelectrogens to electrodes; hence, other microbes' electron transport methods will be studied as well. Furthermore, genetic modifications can significantly improve the efficiency of rates of exocellular electron transfer. The discovery of microorganisms with conductive pili is suggested; however, such bacteria can create high power densities. Electron transmission from electrodes to bacteria has yet to be discovered. Microorganisms which are capable of extracting electrons from electrodes will be particularly significant in the cathode compartment. Although in-depth research and analyses are required to understand the functions of microorganisms in electron transport processes, OmpB and OmpC, outer membrane multicopper proteins, have been found to play a critical role in Fe(III) oxide reduction.

10 Conclusion

However, the MFCs technology has not yet been developed for commercialization, and this approach is currently only available in the lab. The microorganisms employed in MFCs are known as the MFCs' powerhouses. Only *Shewanella* sp. and *Geobacter* sp. have been discovered to accomplish the transfer of electrons through pili among the various bacteria from exoelectrogens to electrodes. Microorganisms with conductive pili can produce high power densities. Proteins of the c-type such as cytochrome-c and pili are considered crucial in the development of conductive biofilms, which bacteria may generate. MFCs technology plays a vital role in generating energy by removing various types of heavy metals. Nonetheless, with the introduction of biocathodes, this technology became more cost-effective, and MFCs have become the only technique for renewable energy generation, as well as other practical uses. For future success in this technology, selecting and breeding pure exoelectrogens of the best quality, to boost performance by modifying current exoelectrogens, or producing fresh exoelectrogens with the highest electrochemical activity, is crucial.

References

1. HaoYu E, Cheng S, Scott K, Logan B (2007) Microbial fuel cell performance with non-Pt cathode catalysts. J Power Sources 171:275–281
2. Yaqoob AA, Khatoon A, MohdSetapar SH, Umar K, Parveen T, Ibrahim MNM, Ahmad A, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10:819
3. Yaqoob AA, Ibrahim MNM, Umar K (2021) Electrode material as anode for improving the electrochemical performance of microbial fuel cells. In: Energy storage battery systems-fundamentals and applications. IntechOpen
4. Asim AY, Mohamad N, Khalid U, Tabassum P, Akil A, Lokhat D, Siti H (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214:379–389
5. Yaqoob AA, Fadzli FS, Ibrahim MNM, Yaakop AS (2022) Benthic microbial fuel cells: a sustainable approach for metal remediation and electricity generation from sapodilla waste. Inter J Environm Sci Technol 10:1–4
6. Malvankar NS, Lovley DR (2012) Microbial nanowires: a new paradigm for biological electron transfer and bioelectronics. Chemsuschem 5:1039
7. Idris MO, Kim HC, Yaqoob AA, Ibrahim MNM (2022) Exploring the effectiveness of microbial fuel cell for the degradation of organic pollutants coupled with bio-energy generation. Sust Energy Technol Assess 52
8. Yaqoob AA, Ibrahim MNM, Umar K, Bhawani SA, Khan A, Asiri AM, Khan MR, Azam M, AlAmmari AM (2021) Cellulose derived graphene/polyaniline nanocomposite anode for energy generation and bioremediation of toxic metals via benthic microbial fuel cells. Polymers 13:135
9. Yaqoob AA, Parveen T, Umar K, Ibrahim MNM (2020) Role of nanomaterials in the treatment of wastewater: a review. Water 12:495
10. Tor A, Danaoglu N, Arslan G, Cengeloglu Y (2009) Removal of fluoride from water by using granular red mud: batch and column studies. J Hazard Mater 164:271–278
11. Moradi F, Maleki V, Saleh-Ghadimi S, Kooshki F, Gargari BP (2019) Potential roles of chromium on inflammatory biomarkers in diabetes: a systematic. Clin Exp PharmacoloPhysiol 46:975–983
12. Yaqoob AA, Ahmad H, Parveen T, Ahmad A, Oves M, Ismail IM, Qari HA, Umar K, Ibrahim MNM (2020) Recent advances in metal decorated nanomaterials and their various biological applications: a review. Front Chem 8:341
13. Genchi G, Sinicropi MS, Carocci A, Lauria G, Catalano A (2017) Mercury exposure and heart diseases. Int J Environ Res Publ Health 14:74
14. Pandey G, Madhuri S (2014) Heavy metals causing toxicity in animals and fishes. Res J Anim Vet Fish Sci 2:17–23
15. Abbas SZ, Riaz M, Ramzan N, Zahid MT, Shakoori FR, Rafatullah M (2014) Isolation and characterization of arsenic resistant bacteria from wastewater. Braz J Microbiol 45:1309–1315
16. Yaqoob AA, Ibrahim MNM, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) Recent advances in anodes for microbial fuel cells: an overview. Materials 13:2078
17. Ucar D, Zhang Y, Angelidaki I (2017) An overview of electron acceptors in microbial fuel cells. Front Microbiol 8:643
18. Ahmad A, Mohd-Setapar SH, Chuong CS, Khatoon A, Wani WA, Kumar R, Rafatullah M (2015) Recent advances in new generation dye removal technologies: novel search for approaches to reprocess wastewater. RSC Adv 5:30801–30818
19. Ahmad A, Setapar SHM, Yaqoob AA, Ibrahim MNM (2021) Synthesis and characterization of GO-Ag nanocomposite for removal of malachite dye from aqueous solution. Mater Today: Proc
20. Kanwal A, Yaqoob AA, Siddique A, Bhawani SA, Ibrahim MNM, Umar K (2021) Hybrid nanocomposites based on graphene and its derivatives: from preparation to applications. In: Graphene and nanoparticles hybrid nanocomposites: from preparation to applications, p 261

21. Cerrillo M, Viñas M, Bonmatí A (2016) Removal of volatile fatty acids and ammonia recovery from unstable anaerobic digesters with a microbial electrolysis cell. Biores Technol 219:348–356
22. Fadzli FS, Rashid M, Yaqoob AA, Ibrahim MNM (2021) Electricity generation and heavy metal remediation by utilizing yam (Dioscorea alata) waste in benthic microbial fuel cells (BMFCs). Biochem Eng J 172:108067
23. Loman NJ, Constantinidou C, Chan JZ, Halachev M, Sergeant M, Penn CW, Robinson ER, Pallen MJ (2012) High-throughput bacterial genome sequencing: an embarrassment of choice, a world of opportunity. Nat Rev Microbiol 10:599–606
24. Kumar R, Singh L, Zularisam A (2016) Exoelectrogens: recent advances in molecular drivers involved in extracellular electron transfer and strategies used to improve it for microbial fuel cell applications. Renew Sustain Energy Rev 56:1322–1336
25. Cao Y, Mu H, Liu W, Zhang R, Guo J, Xian M, Liu H (2019) Electricigens in the anode of microbial fuel cells: pure cultures versus mixed communities. Microb Cell Fact 18:1–14
26. Kakar R, Rashid M, Hussain RT, Yaakop AS, Bhawani SA (2021) Bioremediation of pollutants and sustainable energy production through bacterial activities in microbial fuel cells: an overview. Asian J Chem 33:253–265
27. Loman N, Constantinidou C, Chan J, Halachev M, Sergeant M, Penn C, Robinson E, Pallen M (2012) Nature reviews. Microbiology. Nat Rev Microbiol 10:599–606
28. Kalathil S, Pant D (2016) Nanotechnology to rescue bacterial bidirectional extracellular electron transfer in bioelectrochemical systems. RSC Adv 6:30582–30597
29. Umar K, Yaqoob AA, Ibrahim MNM, Parveen T, Safian MT-U (2021) Environmental applications of smart polymer composites. In: Smart polymer nanocomposites. Elsevier, pp 295–312
30. Stephen AJ, Rees NV, Mikheenko I, Macaskie LE (2019) Platinum and palladium biosynthesized nanoparticles as sustainable fuel cell catalysts. Front Energy Res 7:66
31. Abbas SZ, Rafatullah M, Ismail N, Syakir MI (2017) A review on sediment microbial fuel cells as a new source of sustainable energy and heavy metal remediation: mechanisms and future prospective. Int J Energy Res 41:1242–1264
32. Yaqoob AA, Ibrahim MNM, Yaakop AS, Umar K, Ahmad A (2021) Modified graphene oxide anode: a bioinspired waste material for bioremediation of Pb2+ with energy generation through microbial fuel cells. Chem Eng J 417:128052
33. Yaqoob AA, Ibrahim MN, Ahmad A, Khatoon A, Setapar SH (2021) Polyaniline-based materials for supercapacitors. In: Handbook of supercapacitor materials: synthesis, characterization, and applications, pp 113–130
34. Gregory KB, Bond DR, Lovley DR (2004) Graphite electrodes as electron donors for anaerobic respiration. Environ Microbiol 6:596–604
35. Bond DR, Lovley DR (2005) Evidence for involvement of an electron shuttle in electricity generation by Geothrix fermentans. Appl Environ Microbiol 71:2186–2189
36. Thrash JC, Coates JD (2008) Direct and indirect electrical stimulation of microbial metabolism. Environ Sci Technol 42:3921–3931
37. Yaqoob AA, Ibrahim MNM, Yaakop AS, Ahmad A (2021) Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. Appl Nanosci 11:1949–1961
38. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S (2020) Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview. BiochemEng J 107779
39. Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C (2021) Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov 101579
40. McClure EE, Chávez ASO, Shaw DK, Carlyon JA, Ganta RR, Noh SM, Wood DO, Bavoil PM, Brayton KA, Martinez JJ (2017) Engineering of obligate intracellular bacteria: progress, challenges and paradigms. Nat Rev Microbiol 15:544–558
41. Gurung I, Spielman I, Davies MR, Lala R, Gaustad P, Biais N, Pelicic V (2016) Functional analysis of an unusual type IV pilus in the Gram-positive Streptococcus sanguinis. Mol Microbiol 99:380–392

42. Carbajosa S, Malki M, Caillard R, Lopez MF, Palomares FJ, Martín-Gago JA, Rodríguez N, Amils R, Fernández VM, De Lacey AL (2010) Electrochemical growth of acidithiobacillus ferrooxidans on a graphite electrode for obtaining a biocathode for direct electrocatalytic reduction of oxygen. Biosens Bioelectron 26:877–880
43. Breuer M, Rosso KM, Blumberger J, Butt JN (2015) Multi-haem cytochromes in Shewanella-laoneidensis MR-1: structures, functions and opportunities. J R Soc Interface 12:20141117
44. Strycharz SM, Glaven RH, Coppi MV, Gannon SM, Perpetua LA, Liu A, Nevin KP, Lovley DR (2011) Gene expression and deletion analysis of mechanisms for electron transfer from electrodes to Geobacter sulfurreducens. Bioelectrochemistry 80:142–150
45. Francis CA, O'Mullan GD, Cornwell JC, Ward BB (2013) Transitions in nirS-type denitrifier diversity, community composition, and biogeochemical activity along the Chesapeake Bay estuary. Front Microbiol 4:237
46. Guan Y, Li W, Gong Y, Liu G, Zhang X, Chen J, Gelb J, Yun W, Xiong Y, Tian Y (2011) Analysis of the three-dimensional microstructure of a solid-oxide fuel cell anode using nano X-ray tomography. J Power Sour 196:1915–1919
47. Guan Y, Gong Y, Li W, Gelb J, Zhang L, Liu G, Zhang X, Song X, Xia C, Xiong Y (2011) Quantitative analysis of micro structural and conductivity evolution of Ni-YSZ anodes during thermal cycling based on nano-computed tomography. J Power Sour 196:10601–10605
48. Peng H, Ouyang Y, Bilal M, Wang W, Hu H, Zhang X (2018) Identification, synthesis and regulatory function of the N-acylated homoserine lactone signals produced by pseudomonas chlororaphis HT66. Microb Cell Fact 17:1–11
49. Liu W, Yuan H, Yang J, Li B (2009) Characterization of bioflocculants from biologically aerated filter backwashed sludge and its application in dying wastewater treatment. Biores Technol 100:2629–2632
50. Zhang E, Cai Y, Luo Y, Piao Z (2014) Riboflavin-shuttled extracellular electron transfer from enterococcus faecalis to electrodes in microbial fuel cells. Can J Microbiol 60:753–759
51. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S, Ahmad A (2021) Preparation, characterization, and application of modified carbonized lignin as an anode for sustainable microbial fuel cell. Process Saf Environ Prot 155:49–60
52. Yaqoob AA, Ibrahim MNM, Umar K (2021) Biomass-derived composite anode electrode: synthesis, characterizations, and application in microbial fuel cells (MFCs). J Environ Chem Eng 9:106111
53. Wrighton K, Thrash J, Melnyk R, Bigi J, Byrne-Bailey K, Remis J, Schichnes D, Auer M, Chang C, Coates J (2011) Evidence for direct electron transfer by a gram-positive bacterium isolated from a microbial fuel cell. Appl Environ Microbiol 77:7633–7639
54. Parameswaran P, Bry T, Popat SC, Lusk BG, Rittmann BE, Torres CI (2013) Kinetic, electrochemical, and microscopic characterization of the thermophilic, anode-respiring bacterium Thermincola ferriacetica. Environ Sci Technol 47:4934–4940
55. Daud NNM, Ahmad A, Yaqoob AA, Ibrahim MNM (2021) Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. Environ Sci Pollut Res 28:62816–62827
56. Malone JG, Jaeger T, Manfredi P, Dötsch A, Blanka A, Bos R, Cornelis GR, Häussler S, Jenal U (2012) The YfiBNR signal transduction mechanism reveals novel targets for the evolution of persistent pseudomonas aeruginosa in cystic fibrosis airways. PLoS Pathogens 8:e1002760
57. Ishii SI, Watanabe K, Yabuki S, Logan BE, Sekiguchi Y (2008) Comparison of electrode reduction activities of Geobactersulfurreducens and an enriched consortium in an air-cathode microbial fuel cell. Appl Environ Microbiol 74:7348–7355
58. Yaqoob SB, Bhawani SA, Ismail Abdulrahman RM (2021) Utilization of mangifera Indica as substrate to bioremediate the toxic metals and generate the bioenergy through a single-chamber microbial fuel cell. J Chem 2021
59. Fadzli FS, Bhawani SA, Mohammad REA (2021) Microbial fuel cell: recent developments in organic substrate use and bacterial electrode interaction. J Chem 2021
60. Adebule A, Aderiye B, Adebayo A (2018) Improving bioelectricity generation of microbial fuel cell (MFC) with mediators using kitchen waste as substrate. Ann Appl Microbiol Biotechnol J 2:1008

61. Chuo SC, Mohamed SF, MohdSetapar SH, Ahmad A, Jawaid M, Wani WA, Yaqoob AA, Ibrahim MNM (2020) Insights into the current trends in the utilization of bacteria for microbially induced calcium carbonate precipitation. Materials 13:4993
62. Yu Z, Peng L, Wang X-B, Sun Y-P (2012) Influence of initial biofilm growth on electrochemical behavior in dual-chambered mediator microbial fuel cell. J Fuel Chem Technol 40:967–972
63. Fan L-P, Xue S (2016) Overview on electricigens for microbial fuel cell. Open Biotechnol J 10
64. Liu J, Yong Y-C, Song H, Li CM (2012) Activation enhancement of citric acid cycle to promote bioelectrocatalytic activity of arcA knockout Escherichia coli toward high-performance microbial fuel cell. ACS Catal 2:1749–1752
65. Samrot AV, Senthilkumar P, Pavankumar K, Akilandeswari G, Rajalakshmi N, Dhathathreyan K (2010) Electricity generation by Enterobacter cloacae SU-1 in mediator less microbial fuel cell (Retraction of vol 35, pg 7723. Int J Hydrog Energy 37(2012):728–728
66. Singh L, Siddiqui MF, Ahmad A, Rahim MHA, Sakinah M, Wahid ZA (2013) Biohydrogen production from palm oil mill effluent using immobilized mixed culture. J Ind Eng Chem 19:659–664
67. Bolat P, Thiel C (2014) Hydrogen supply chain architecture for bottom-up energy systems models. Part 2: techno-economic inputs for hydrogen production pathways. Int J Hydrog Energy 39:8898–8925
68. Prasad D, Arun S, Murugesan M, Padmanaban S, Satyanarayanan R, Berchmans S, Yegnaraman V (2007) Direct electron transfer with yeast cells and construction of a mediatorless microbial fuel cell. Biosens Bioelectron 22:2604–2610
69. Lwalaba JLW, Zvobgo G, Fu L, Zhang X, Mwamba TM, Muhammad N, Mundende RPM, Zhang G (2017) Alleviating effects of calcium on cobalt toxicity in two barley genotypes differing in cobalt tolerance. Ecotoxicol Environ Saf 139:488–495
70. Jiang Y, Ulrich AC, Liu Y (2013) Coupling bioelectricity generation and oil sands tailings treatment using microbial fuel cells. Biores Technol 139:349–354
71. Huang L, Chen J, Quan X, Yang F (2010) Enhancement of hexavalent chromium reduction and electricity production from a biocathode microbial fuel cell. Bioprocess Biosyst Eng 33:937–945
72. Li F, Jin C, Choi C, Lim B (2019) Simultaneous removal and/or recovery of Cr (VI) and Cr (III) using a double MFC technique. Environ EngManag J (EEMJ) 18
73. Ryu E-Y, Kim M-A, Lee S-J (2011) Characterization of microbial fuel cells enriched using Cr(VI)-containing sludge. J Microbiol Biotechnol 21:187–191
74. Huang L, Zhou P, Quan X, Logan BE (2018) Removal of binary Cr(VI) and Cd(II) from the catholyte of MFCs and determining their fate in EAB using fluorescence probes. Bioelectrochemistry 122:61–68
75. Wang G, Huang L, Zhang Y (2008) Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotech Lett 30:1959–1966
76. Zhang B, Feng C, Ni J, Zhang J, Huang W (2012) Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J Power Sour 204:34–39
77. Vickers NJ (2017) Animal communication: when i'm calling you, will you answer too? Curr Biol 27:R713–R715
78. Choi C, Cui Y (2012) Recovery of silver from wastewater coupled with power generation using a microbial fuel cell. Biores Technol 107:522–525
79. Nancharaiah Y, Mohan SV, Lens P (2015) Metals removal and recovery in bioelectrochemical systems: a review. Biores Technol 195:102–114
80. Abourached C, Catal T, Liu H (2014) Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Res 51:228–233
81. Zhang B-G, Zhou S-G, Zhao H-Z, Shi C-H, Kong L-C, Sun J-J, Yang Y, Ni J-R (2010) Factors affecting the performance of microbial fuel cells for sulfide and vanadium (V) treatment. Bioprocess Biosyst Eng 33:187–194

82. Tandukar M, Tezel U, Pavlostathis SG (2009) Biological chromium (VI) reduction in microbial fuel cell: a three in one approach. Proc Water Environ Fed 2009:527–535
83. Burscher B, van Spanje J, de Vreese CH (2015) Owning the issues of crime and immigration: the relation between immigration and crime news and anti-immigrant voting in 11 countries. Elect Stud 38:59–69
84. Wu B, Chen Z (2011) An integrated physical and biological model for anaerobic lagoons. Biores Technol 102:5032–5038
85. Ya F, Wei-da W, Xin- T, Hao-ran L, Zhuwei D, Zhi Y, Yun-long D (2014) Isolation and characterization of an electrochemically active and cyanide-degrading bacterium isolated from a microbial fuel cell. RSC Adv 4:36458–36463
86. Singhvi P, Chhabra M (2013) Simultaneous chromium removal and power generation using algal biomass in a dual chambered salt bridge microbial fuel cell. J Bioremed Biodegrad 4
87. Li Y, Lu A, Ding H, Jin S, Yan Y, Wang C, Zen C, Wang X (2009) Cr(VI) reduction at rutile-catalyzed cathode in microbial fuel cells. Electrochem Commun 11:1496–1499
88. Gai R, Liu Y, Liu J, Yan C, Jiao Y, Cai L, Zhang L (2018) Behavior of copper, nickel, cadmium and mercury ions in anode chamber of microbial fuel cells. Int J Electrochem Sci 13:3050–3062
89. Modin O, Wang X, Wu X, Rauch S, Fedje KK (2012) Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions. J Hazard Mater 235:291–297
90. Choi C, Hu N (2013) The modeling of gold recovery from tetrachloroaurate wastewater using a microbial fuel cell. Biores Technol 133:589–598
91. Wang Z, Lim B, Choi C (2011) Removal of Hg2+ as an electron acceptor coupled with power generation using a microbial fuel cell. Biores Technol 102:6304–6307
92. Liu Y, Song P, Gai R, Yan C, Jiao Y, Yin D, Cai L, Zhang L (2019) Recovering platinum from wastewater by charring biofilm of microbial fuel cells (MFCs). J Saudi Chem Soc 23:338–345
93. Huang L, Li T, Liu C, Quan X, Chen L, Wang A, Chen G (2013) Synergetic interactions improve cobalt leaching from lithium cobalt oxide in microbial fuel cells. Biores Technol 128:539–546
94. Abbas SZ, Rafatullah M, Ismail N, Syakir MI (2016) Removal of metals (chromium and copper) and power generation through sediment microbial fuel cell. Int J Env Tech Sci 2:56–60
95. Tao H-C, Liang M, Li W, Zhang L-J, Ni J-R, Wu W-M (2011) Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. J Hazard Mater 189:186–192
96. Kumar R, Singh L, Zularisam A, Hai FI (2018) Microbial fuel cell is emerging as a versatile technology: a review on its possible applications, challenges and strategies to improve the performances. Int J Energy Res 42:369–394
97. Luo S, Wu X, Jiang H, Yu M, Liu Y, Min A, Li W, Ruan R (2019) Edible fungi-assisted harvesting system for efficient microalgae bio-flocculation. Biores Technol 282:325–330
98. Habibul N, Hu Y, Sheng G-P (2016) Microbial fuel cell driving electrokinetic remediation of toxic metal contaminated soils. J Hazard Mater 318:9–14
99. Wang Z, Zhang B, Jiang Y, Li Y, He C (2018) Spontaneous thallium (I) oxidation with electricity generation in single-chamber microbial fuel cells. Appl Energy 209:33–42
100. Hamilton WP, Kim M, Thackston EL (2005) Comparison of commercially available Escherichia coli enumeration tests: implications for attaining water quality standards. Water Res 39:4869–4878
101. Xiao L, He Z (2014) Applications and perspectives of phototrophic microorganisms for electricity generation from organic compounds in microbial fuel cells. Renew Sustain Energy Rev 37:550–559
102. Pandit S, Khilari S, Roy S, Pradhan D, Das D (2014) Improvement of power generation using Shewanella putrefaciens mediated bioanode in a single chambered microbial fuel cell: effect of different anodic operating conditions. Biores Technol 166:451–457
103. Xing D, Zuo Y, Cheng S, Regan JM, Logan BE (2008) Electricity generation by Rhodopseudomonas palustris DX-1. Environ Sci Technol 42:4146–4151

104. Qiao Y, Li CM, Bao S-J, Lu Z, Hong Y (2008) Direct electrochemistry and electrocatalytic mechanism of evolved Escherichia coli cells in microbial fuel cells. Chem Commun 1290–1292
105. Raghavulu SV, Goud RK, Sarma P, Mohan SV (2011) Saccharomyces cerevisiae as anodic biocatalyst for power generation in biofuel cell: influence of redox condition and substrate load. Biores Technol 102:2751–2757
106. Hirayama H, Suzuki Y, Abe M, Miyazaki M, Makita H, Inagaki F, Uematsu K, Takai K (2011) Methylothermussubterraneus sp. nov., a moderately thermophilic methanotroph isolated from a terrestrial subsurface hot aquifer. Int J Syst Evolut Microbiol 61:2646–2653
107. Li X, Zhong G-Z, Qiao Y, Huang J, Hu WH, Wang X-G, Li CM (2014) A high performance xylose microbial fuel cell enabled by Ochrobactrum sp. 575 cells. RSC Adv 4:39839–39843
108. Nandy A, Kumar V, Kundu PP (2013) Utilization of proteinaceous materials for power generation in a mediatorless microbial fuel cell by a new electrogenic bacteria Lysinibacillus sphaericus VA5. Enzyme Microb Technol 53:339–344
109. Cui Y, Rashid N, Hu N, Rehman MSU, Han J-I (2014) Electricity generation and microalgae cultivation in microbial fuel cell using microalgae-enriched anode and bio-cathode. Energy Convers Manag 79:674–680
110. Inglesby AE, Beatty DA, Fisher AC (2012) Rhodopseudomonas palustris purple bacteria fed Arthrospira maxima cyanobacteria: demonstration of application in microbial fuel cells. RSC Adv 2:4829–4838
111. Yuan Y, Chen Q, Zhou S, Zhuang L, Hu P (2011) Bioelectricity generation and microcystins removal in a blue-green algae powered microbial fuel cell. J Hazard Mater 187:591–595
112. Zhang J, Tang Y, Song C, Xia Z, Li H, Wang H, Zhang J (2008) PEM fuel cell relative humidity (RH) and its effect on performance at high temperatures. Electrochim Acta 53:5315–5321
113. Freguia S, Tsujimura S, Kano K (2010) Electron transfer pathways in microbial oxygen biocathodes. Electrochim Acta 55:813–818
114. Ong SP, Jain A, Hautier G, Kang B, Ceder G (2010) Thermal stabilities of delithiated olivine MPO4 (M = Fe, Mn) cathodes investigated using first principles calculations. Electrochem Commun 12:427–430
115. Birloaga I, Veglio F (2018) Overview on hydrometallurgical procedures for silver recovery from various wastes. J Environ Chem Eng 6:2932–2938
116. Zhang P-Y, Liu Z-L (2010) Experimental study of the microbial fuel cell internal resistance. J Power Sour 195:8013–8018
117. Arvay A, Yli E, Liu C-H, Peng X-H, Koski P, Cindrella L, Kauranen P, Wilde P, Kannan AM (2012) Characterization techniques for gas diffusion layers for proton exchange membrane fuel cells—A review. J Power Sour 213:317–337
118. Yaqoob AA, Ibrahim MNM, Ahmad A, Reddy AVB (2021) Toxicology and environmental application of carbon nanocomposite. In: Environmental remediation through carbon based nano composites. Springer, pp 1–18
119. Yaqoob AA, Umar K, Adnan R, Ibrahim MNM, Rashid M (2021) Graphene oxide–ZnO nanocomposite: an efficient visible light photocatalyst for degradation of rhodamine B. Appl Nanosci 11:1291–1302
120. Kim C, Lee CR, Song YE, Heo J, Choi SM, Lim D-H, Cho J, Park C, Jang M, Kim JR (2017) Hexavalent chromium as a cathodic electron acceptor in a bipolar membrane microbial fuel cell with the simultaneous treatment of electroplating wastewater. Chem Eng J 328:703–707
121. Kilicarslan A, Saridede M, Stopić S, Friedrich B (2013) Recovery of copper and zinc from brass wastes via ionic liquid leach. In: European metallurgical conference, pp 1167–1172
122. Yaqoob AA, Noor M, Serrà A, Ibrahim MNM (2020) Advances and challenges in developing efficient graphene oxide-based ZnO photocatalysts for dye photo-oxidation. Nanomaterials 10:932
123. Yaqoob AA, Serrà A, Ibrahim MNM, Yaakop AS (2021) Self-assembled oil palm biomass-derived modified graphene oxide anode: an efficient medium for energy transportation and bioremediating Cd(II) via microbial fuel cells. Arab J Chem 14:103121

124. Yaqoob AA, Ibrahim MNM, Yaakop AS (2021) Application of oil palm lignocellulosic derived material as an efficient anode to boost the toxic metal remediation trend and energy generation through microbial fuel cells. J Clean Prod 314:128062
125. Yaqoob AA, Umar K, Ibrahim MNM (2020) Silver nanoparticles: various methods of synthesis, size affecting factors and their potential applications—A review. Appl Nanosci 10:1369–1378
126. Liu C, Shi W, Li H, Lei Z, He L, Zhang Z (2014) Improvement of methane production from waste activated sludge by on-site photocatalytic pretreatment in a photocatalytic anaerobic fermenter. Biores Technol 155:198–203
127. Ayotamuno M, Kogbara R, Ogaji S, Probert S (2006) Petroleum contaminated ground-water: remediation using activated carbon. Appl Energy 83:1258–1264
128. Ezziat L, Elabed A, Ibnsouda S, El Abed S (2019) Challenges of microbial fuel cell architecture on heavy metal recovery and removal from wastewater. Front Energy Res 7:1

The Potential Benefits of Microbial Fuel Cells in the Context of the Sustainable Development Goals

Abubakari Zarouk Imoro, Nana Aboagye Acheampong, Seth Oware, Henk Okrah, Vincent Tofio Coulibaly, Abdul Ganiyu Ali, Francis Asare-Amegavi, Donatus Krah, and Felix Offei

Abstract The microbial fuel cell is a versatile technology that belongs to the broad category of technology referred to as microbial electrochemical systems. It has the potential to treat wastewater and produce electricity. In some instances, it has been used for hydrogen gas production, nitrate removal, algae cultivation, and heavy metal reduction. The bioelectricity potential of the technology is promising and has been explored in biosensors and related devices. The diverse applications of the MFC technology makes it a commendable technology for sustainable development. Thus, it's potential to support the achievement of some sustainable development goals has been discussed in this chapter. These goals are goal 2 (Sustainable agriculture), goal

A. Z. Imoro (✉)
Department of Environment, Water and Waste Engineering, University for Development Studies, Tamale, Ghana
e-mail: zabubakari@uds.edu.gh

N. A. Acheampong
Department of Microbiology, University for Development Studies, Tamale, Ghana
e-mail: naboagye@uds.edu.gh

S. Oware
Department of Biological Sciences, University for Development Studies, Tamale, Ghana
e-mail: soware@uds.edu.gh

H. Okrah · A. G. Ali · F. Asare-Amegavi
School of Engineering, University for Development Studies, Tamale, Ghana
e-mail: hokrah@uds.edu.gh

A. G. Ali
e-mail: aganiyu@uds.edu.gh

F. Asare-Amegavi
e-mail: famegavi@uds.edu.gh

V. T. Coulibaly · D. Krah
Spanish laboratory Complex, University for Development Studies, Tamale, Ghana
e-mail: vincent.coulibaly@uds.edu.gh

F. Offei
Department of Marine Engineering, Regional Maritime University, Accra, Ghana
e-mail: felix.offei@rmu.edu.gh

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_9

3 (Healthy lives and wellbeing for all), goal 6 (Access to water and sanitation for all), goal 7 (Access to affordable, reliable, sustainable, and modern energy for all), goal 9 (Resilient infrastructure, sustainable industrialization, and foster innovation), goal 12 (Sustainable production and consumption), goal 13 (Combat climate change), goal 14 (Protect life under water), and goal 15 (Protect life on land). Given the outlined potential that this technology has for our sustainable development, it is recommended that considerable funding is provided for extensive research on how to improve the efficiency of the technology for commercialization.

1 Introduction

Sustainable development is that type of development that seeks to satisfy the needs of both present and future generation without compromising on environmental quality [62]. To achieve this ambitious agenda, goals must be set and all nations must work towards the achievement of the set goals. In respect of this, members of the United Nations have agreed upon 17 goals and various measures are being put in place towards the realization of these goals. These include policy revision, technological changes/improvements, behavioral changes, and political and intergovernmental actions. Among promising technologies that can contribute to the achievement of most of the sustainable development goals (SDGs) is the microbial fuel cell (MFC). Out of the 17 SDGs, MFCs have the potential to contribute directly to the achievement of 9 of the goals (Fig. 1). MFC is a technology that converts chemical energy in wastewater into electricity [65]. It has several applications as discussed in the

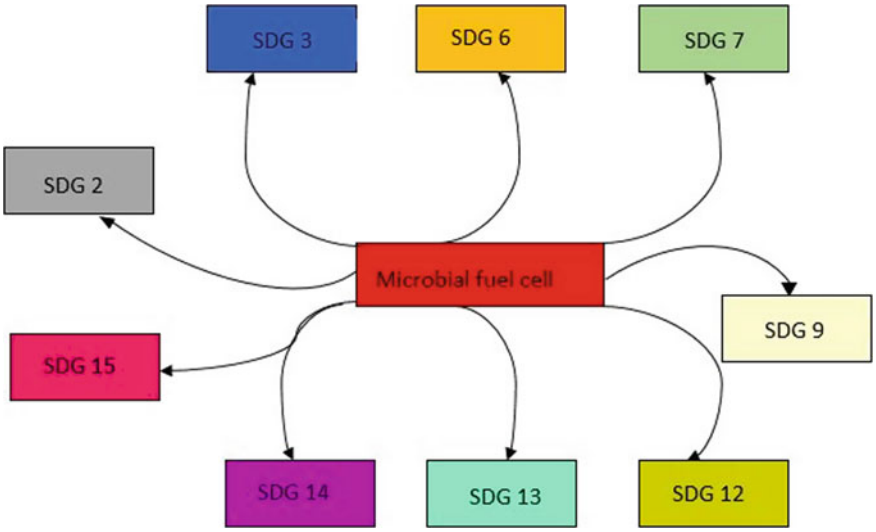

Fig. 1 SDGs that MFCs have the potentials to contribute to their realisation

sections below. Though a very versatile technology, it is yet to reach commercial use because of some operational challenges detailed in [20]. This chapter presents the potential benefits the MFC technology can offer to the world when commercialized.

2 Microbial Fuel Cell for Sustainable Agriculture (SDG 2)

2.1 Treatment of Wastewater with MFC for Irrigation

Water is essential for the proper growth and development of living organisms. Wastewater usually has low oxygen content and transports various microbial pathogens to crops and animals. MFCs treat wastewater [5] to acceptable levels. In some cases, by combining the potential of some algae to utilize carbon dioxide and produce oxygen [13], MFCs have been used for algae production. *Chlamydomonas reinhardtii* and *Chlorella* sp. have been assessed for their abilities to support electricity production and have been employed fairly in wastewater treatment [13]. The electrical energy, so generated from MFCs, can be used to power some farm implements (i.e., water pumps) for the improvement of agriculture output in places with poor electricity supply [52]. Excessive boron in irrigation water could deteriorate plant health [42]. An anion-exchange membrane MFC was able to remove 40–50% of boron during pre-treatment of water and removed 80–90% of boron during the post-treatment process [42]. The effluent produced met the requirement of water used in irrigation [42], thereby, underlining the potential of MFC technology for the treatment of contaminated water for reuse [67]. The MFC technology's potential for the estimation of hunger, the achievement of food security, and improving nutrition and sustainable agriculture should be considered and exploited to support the realization of the generality of human wellbeing.

2.2 Safeguarding Food Security Using MFC

Biofuel has been proposed as an alternative to fossil fuels [29] in terms of its ability to produce environmentally friendly residues [8]. The dependence on first-generation biofuels, which rely on crop plants as feedstock, has raised food security concerns. MFC technologies that rely on agricultural waste, algae-based technology, among others can be used to generate electricity and fertilizer for farming [9, 44]. These technologies will rely on second- and third-generation biofuel energy sources to generate energy thereby reducing the potential burden that such energy generation schemes (biofuels) may place on food production, availability, and access.

Reliance on waste from food crops such as soy, rice, maize, and sugarcane, among others as primary substrates for microbial electrogens will reduce the need to spend massively on cultivating such crops for energy purposes [46]. This approach could

help mitigate food insecurity [46]. Sustainable agriculture promises to be a backbone of bioenergy generation by providing raw material (organic waste) for bioelectrochemical systems [11]. The organic matter produced as residues from MFCs could also be used to improve (fertilize) crop yield, thereby improving food security [46].

2.3 Management of Agricultural Waste Using MFC

Produce from agriculture is used to feed humans and animals worldwide generating large quantities of waste in the process. Agricultural waste, food waste, and hazardous waste are major solid wastes obtained as unavoidable by-products of agricultural activities globally [56]. Agricultural waste, most of which is organic in nature, is projected to increase due to the increasing use of intensive farming methods [6]. Bioenergy technologies such as MFCs could help manage these large volumes of residues and also produce electricity in the process [6]. Microorganisms well adapted for harsh conditions often present in composts have been studied and their electrigenicity (ability to generate electricity) fairly assessed. These organisms are employed in the digestion of various kinds of organic matter realized as residues from the activities of agriculture. Archaebacteria, such as *Haloferax volcanii* and *Natrialba magadii*; Acidobacteria, such as *Geothrix fermentans* and *Arcobacter* sp.; Cyanobacteria, such as *Synechococcus elongates* and *Nostoc* sp.; Firmicutes, such as *Clostridium butyricum* and *Thermincola* sp.; Proteobacteria, such as *Rhodospirillum rubrum* and *E. coli;* Yeast, such as *Saccharomyces cerevisiae* and *Arxula adeninivorans;* and Algae, such as *Chlamydomonas reinhardtii* and *Chlorella* sp., have been employed as useful electricigens in various MFCs [13] for the breakdown of organic matter. The breakdown of organic wastes in MFCs often results in the conversion of the waste materials into environmentally friendly safer forms.

3 Health and Wellbeing Promotion (SDG 3)

The insanitary management of wastewater creates enabling environments for the spread of diseases including malaria. Stagnant water in particular promotes the growth of Anopheles mosquitoes that are responsible for malaria. Also, when fecal sludge is not treated before discharge, several bacterial, fungi, protozoan, and viral diseases can be spread leading to an incapacitated population and by extension, economy. MFCs have proved to be capable of treating high-strength wastewater [5] thus can reduce the incidences of pollution often resulting from poor handling of industrial wastewater.

Also, poor wastewater handling reduces the esthetic quality of the environment aside the fact that the environment is polluted and ecosystems are disturbed. A clean environment promotes wellbeing. Sereneness promotes emotional balance and inner

peace [21] and these are important factors for an individual's wellbeing. Also, the presence of a clean environment and clean air for breathing reduces the chances of one falling ill. Clean environments are known to help convalescence recover quickly from ill-health [55]. Moreover, MFCs can help reduce pollution resulting from the use of fossil fuels. The release of CO_X, NO_X, and SO_X from fossil fuel use can lead to disease conditions associated with cardiovascular disorders. Unfortunately, these gases can be transported further away from polluting sources and cause harm to all forms of biota. MFCs provide renewable energy with no external carbon emission [20]. It is therefore beneficial for use in the construction of safe and sustainable infrastructures (planned settlements, hospitals, recreation centers) that are necessary for our wellbeing.

4 Water and Sanitation for All (SDG 6)

Conventional water treatment facilities are high-energy consumers. In the USA, for example, they account for an approximated 116.07–145.08 out of the 2,901.67 USD/MWh costs of electricity production using a 10% discount on "levelised" cost of electricity generation [28]. This high-energy consumption of conventional water treatment plants increases their carbon footprints and also, may limit their profit margins. Suitable alternative energy sources are thus needed to reduce the reliance on fossil fuel-based ones. The MFC technology is one promising choice, especially because it supports cyclic economy by converting waste into energy and other resources (ie, manure). MFCs may be used as a standalone source or supplementary energy source for conventional wastewater treatment plants. Some researchers have recorded high COD and BOD reductions (see subsequent sections) that make this technology a candidate for wastewater reuse and thus can promote environmental sanitation. Across the world, large volumes of domestic wastewater are generated and discharged, sometimes without any form of treatment. For instance, in Ghana, less than 8% of domestic wastewater generated are treated [64]. Meanwhile, treated domestic wastewater can at least be used for irrigation purposes or discharged into wetlands to support the biodiversity of wetlands.

Also, groundwater resources are abundant in many parts of the world and are relatively safer to use compared to surface waters. They usually require no treatment at all, especially in less industrial and agricultural environments. However, because of the need for energy to pump groundwater for use, their availability in remote areas in the developing world is limited. MFCs have the potential to overcome the "energy-need barrier" of electric powered boreholes. It is relatively easier to assemble and detach. Fully functional MFCs can serve as sustainable batteries for electric powered boreholes in remote areas not connected to national grids. With reduced energy cost, the availability of clean water for the observation of good sanitary practices (cleaning and maintenance) will most likely increase and thus reduce the incidences of disease outbreaks related to poor sanitation. MFCs can also be used to treat fecal sludge and therefore contribute to the safe management of human waste.

5 Affordable, Reliable, Sustainable, Modern Energy for All (SDG 7)

The energy produced from MFCs is from the chemical energy stored in the organic fraction of solid waste and wastewater. Thus, the energy from MFCs can comparably be more affordable than fossil and thermal-based sources. The initial cost of constructing MFCs can be high but considering the fact that the source of energy is from waste, it has a long-term benefit including the improvement of environmental quality. Biohydrogen can also be produced from MFCs [20]. Hydrogen is a cleaner source of energy (no carbon emissions) that can be made more affordable with the use of MFCs. Since MFCs are comparably easier to assemble, they can be set up in remote areas for biohydrogen production to support electricity generation and thus reducing the need for connection to national grids. The high cost of extending electricity from the national grid to remote areas is one of the main reasons why a number of remote communities live without electricity in the developing world. When cheaper, simple, and more efficient electrode materials, membranes, and catholytes are developed, MFCs will have the additional advantage of being easy to operate and maintain and thus be a more sustainable source of energy. So far as humans exist, organic waste will be produced. This presents some assurance of the continuous availability of sources of raw materials for the running of MFCs for affordable energy. Also, MFCs with microalgae as terminal electron (O_2) producers in the cathode chamber have the additional benefits of producing algal biomass, which can be used for biodiesel production [30]. Biodiesel can be used as an alternative to natural gas and diesel for the running of engines.

6 Resilient Infrastructure, Sustainable Industrialization, and Innovation (SDG 9)

MFCs have several applications including use for nutrient recovery [65], heavy metal reduction [59], biohygrogen production [33], and as biosensors [14]. It is a technology that allows for innovation in many aspects of science and technology. It occupies a relatively small space, thus is appropriate in this era and for the future as land space is continuously becoming a limited resource. Wastewater treatment plants such as stabilization ponds occupy large areas of land but traditionally perform one function (wastewater treatment). Meanwhile, MFCs per their designs will occupy relatively small areas of land and besides wastewater treatment, produce electricity, and several other products including biohydrogen and algal biomass. Currently, industrial development is on the trajectory of efficiency and low carbon footprints. Industries that are interested in clean and affordable energy will find MFCs as ideal alternatives or supplementary energy sources to promote the eco-friendliness of their business through cuts in carbon emissions.

7 Usefulness of MFCs for Achieving SDGs 12, 13, 14, and 15

This section discusses three SDGs together because of the cross-cutting nature of the usefulness of the MFC technology to these goals.

7.1 MFC as Biosensors to Monitor Pollution

Generally, a sensor is a device that measures physical variables such as temperature, pressure, mass, light, humidity, and strain. It then converts the measured variable into an accessible signal, usually an electric signal, by a transducer. The electric signal generated is transferred to a microprocessor that translates it into a meaningful reading to be displayed [68]. Sensors require power for their functionality. Many sensors have a battery as their main power source. Power is needed for data processing and communication. Sensors use a communication system as they can be in a remote area or at a non-accessible location of the equipment. Data transmission can be costly in terms of energy consumption, the energy required depends on the specific sensor category. Gas sensors require a higher amount of energy compared to image, temperature, and pressure sensors [45].

Battery-powered sensors come with their limitations as the batteries have to be replaced or recharged. Self-powered sensors can help overcome this challenge as they can harvest the needed power for sensing, computing, storage, and communication. The power needed can be harvested from the signal being sensed or from other energy sources like solar energy and ambient vibrations. This provides a reliable and sustainable means of monitoring and assessment [47]. An MFC-based biosensor is a self-powered device that can run for a long period. The device is user-friendly, cost-friendly, easy to install, and reusable [40]. MFC-based biosensors can be used for various applications like water quality monitoring (such as biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), microbial activity, and heavy metals monitoring in wastewater and monitoring of air quality. These are all parameters that are useful in assessing how far SDGs 12, 13, 14, and 15 have been achieved. The operational mechanism of an MFC-based biosensor is such that it measures the analyte of interest and gives a corresponding response to its output electrical current, without the need for a transducer. The sensing step is integrated with the electrical signal transition step. This gives it a fast response time [53]. With this technology, proper environmental monitoring can be done for example concerning industrial water effluents. This will ensure effluents released into the environment are meeting the required standards and are not affecting life under water directly or indirectly (SDG 14). With MFC-based biosensors being self-powered, monitoring can be done in remote areas (e.g., Benthic regions) and for long periods. This can help check and ensure responsible behavioral practices from producers and end-users (SDG 12). Sediment microbial fuel cell (SMFC) is a proven application

of MFC-based biosensor. Under appropriate working conditions, SMFCs generate electrical energy by oxidizing organic matter [34]. This technology has been used in the aquatic environment for the monitoring of temperature [70], dissolved oxygen concentrations [51], and water quality including pH, electrical conductivity, Cl^-, K^+, $NO_3^{-\cdot}$ and SO_4^{2-} [57] in remote areas. With SMFC, monitoring of seawater/ocean floor can be done (SDG 14).

7.2 MFC for Bioremediation

The application of MFCs for the remediation of various organic and inorganic environmental pollutants is an area of interest as it can help many manufacturing and processing industries manage waste generated from their processes [35] (SDG 12). Studies show that MFCs can be used for the effective degradation of antibiotics (e.g., chloramphenicol, sulphamethoxazole, acetaminophen), phenolic compounds (e.g., 2,4-dichlorophenol, p-nitrophenol, 4-chlorophenol), synthetic dye (e.g., azo dye, methyl orange, monoazo dye, congo red), nitrogen-based compounds (e.g., pyridine, ammonium), organic solvents (e.g., ethyl acetate, toluene), polycyclic aromatic hydrocarbons, pesticide, perchlorate, sulfur, emerging contaminants (e.g., bisphenol A, estrone, sulfamethazine, triclocarban), and trace organic compounds (e.g., atenolol, trimethoprim, naproxen, ibuprofen, caffeine, dilantin, norfluoxetine, diclofenac, cimetidine) [35]. With the wide application of this technology, responsible and environmentally friendly management of waste by industries including food processing, textile, pharmaceutical, plastic, petrochemical, refinery, printing, leather, detergent manufacturing, and mining industries can be achieved. The production and use of fossil fuels come with a lot of environmental threats that need to be addressed. One of such threats that cannot be overlooked is oil spillage. MFC technology can be utilized for the biodegradation of hydrocarbons (Oils spills). It has been used in the biodegradation of hydrocarbon-contaminated sediments [39], phenanthrene, and benzene in aqueous systems [4] (SDG 14) and petroleum hydrocarbons in saline soils [32]. As such, MFCs can be explored as a technology for oil spill cleanup either in combination with other methods or independently. This offers effective cleanup while reducing the risk of secondary pollution. Also, an added benefit of using MFC for oil spill cleanup can be the use of power generated from MFC for powering power-consuming cleanup activities.

8 MFC for the Production of Renewable Energy

8.1 Power Generation from Wastewater Using MFC

Currently, fossil fuels are a major source of energy [41]. With fossil fuels being non-renewable, the world is burdened with possible exhaustion of this resource and environmental pollution challenges that come with the use of fossil fuels. The combustion of fossil fuels to generate electricity contributes to about 40% of global CO_2 emissions, which is a major contributing factor to global warming [2]. The effects of global warming go beyond an increase in average temperature. Plants' and animals' extinction, rise in global sea levels and ocean acidification, and attack on food and water security among others are all threats facing our world. Climate change today is a pressing challenge and a collective effort is thus required to help reduce emissions of CO_2 and other greenhouse gases from human activities. To ensure a responsible development, there is a need for us to move towards sustainable ways of producing energy. Already, renewable energy sources such as wind energy, solar energy, geothermal power, and biomass energy are currently being explored and are fast-growing [19]. According to the International Energy Agency (IEA) [27], 29% of electricity generated globally was from renewables. Similarly, the microbial fuel cell technology is an alternative technology for energy production as it can convert the chemical energy of organic compounds into electrical energy, while reducing carbon footprint and environmental pollution (SDG 13). The power generation process of MFC is clean, reliable, and efficient as it utilizes renewable methods and does not generate any toxic by-products [15]. The MFC technology can be applied to a wide range of waste sources, including solid waste and wastewater, from domestic and various manufacturing and processing industries such as agriculture, food processing, oil, and mining. With waste sources being readily available, power can be generated all year-round and at a relatively low cost (SDG 12). Considering the benefits of MFC as a power generation alternative, there is the need to explore this technology and commercialize it [15].

8.2 Power Generation from Methane Using MFC

Over the years, several technologies have been used to produce electricity from methane [22]. Fortunately, methane can be available in large quantities and there is the need to explore ways of capturing, storing, and safer ways of generating power from it. This will provide sustainable means of generating power, while mitigating the environmental threat methane poses. Globally, methane emissions from natural sources and human activities are estimated to be in hundreds of million tonnes [26]. Agriculture is considered the main source of methane emissions followed by the energy sector. Other sources include stationary and mobile waste combustion. Methane is a more potent greenhouse gas compared to CO_2 and also affects air quality making

it a dangerous air pollutant [26]. The main difficulty with the biological conversion of methane to electricity has been finding suitable microbes for effective anaerobic CH_4 oxidation. Though biological conversion of methane to power with MFC technology has its challenges, conventional technologies such as gas-turbine generators and conversion of methane to liquid fuel are capital intensive [31]. Previous studies have shown that a sustainable and considerable amount of electricity can be generated in MFCs using specific microbes and a combination of selected microbes [31]. The use of external electron carriers and increasing acid concentrations proved to increase current generation and power density. Moreover, MFC technology offers flexibility in operations and provides the ability to integrate with other processes. A two-staged system, where methane is initially converted to liquid fuel, like methanol, and then followed by electricity generation, using methanol as substrate in an MFC has proven to generate maximum power density [31]. MFC has a promising future concerning energy production from methane (SDG 13). Also, with methane being available in large quantities all year-round, it can serve as a sustainable source of energy that supports the MFC technology to perform better. This will help meet the growing global energy demands with a more responsible approach.

8.3 MFC for Biohydrogen Production

Biohydrogen can be produced from microbial electrolysis cells coupled with MFC (MEC–MFC). This technology offers a sustainable and clean way of producing hydrogen. Currently, the majority of global industrial hydrogen production is based on fossil fuels like oil, natural gas, and coal [10]. MEC–MFC accomplishes the production of biohydrogen by combining electrolysis and MFC technology for the conversion of organic materials from biodegradable wastes to high-purity hydrogen [54]. Electrolysis is performed in the MEC, whereas electricity for the electrolysis is supplied by the MFC. Conventional methods for hydrogen production that employ the use of electrolysis have relatively high electricity demand [54]. However, with improved technology in MEC–MFC-coupled systems, hydrogen can be extracted from substrates without extra electricity supply [54] (SDG 12). Hydrogen is extensively used by many industries for a variety of applications. It is mainly used in petroleum refinery processes such as for desulfurization and cracking of oil [22]. Hydrogen is used as a raw material or for the synthesis of chemicals such as methanol, dimethyl ether, cyclohexane, and ammonia [10]. Other industrial uses include astronautics, aeronautics, metallurgy, plastics, steel, electronics and semiconductors, food, and edible oil processing. As the world seeks to move towards clean and renewable energy resources, the use of hydrogen as an energy carrier in fuel cells for generating electricity and as an alternative fuel for vehicles is being heavily explored [10] (SDG 12). Compared to fossil-based fuels, hydrogen has higher mass energy [60]. Moreover, it does not contain any traces of carbon making it environmentally friendly [1]. This would help solve the problem of greenhouse gase emissions from vehicles (SDG

13). The Intergovernmental Panel on Climate Change (IPCC) [25] report on mitigation of climate change estimated that 23% of total energy-related CO_2 emissions were produced from the transport sector. Studies carried out to explore the feasibility of hydrogen as a potential replacement for fossil fuels showed that hydrogen fuel offers economic savings compared to conventional fuels [50]. Fuel cells convert chemical energy from fuels into electrical energy through electrochemical reactions [38]. Thus, a hydrogen-powered fuel cell will serve as a sustainable technology for powering vehicles. This will help the world's agenda of phasing out fossil-fuel cars to mitigate global warming and climate change (SDG 13).

8.4 MFC for Water Recycling

Water is a major resource for most human activities [43]. These include the use of water for domestic, agricultural, commercial, and industrial purposes. The overall demand for water keeps increasing, contributing to an increased generation of wastewater. Therefore, there is a need to explore new technologies for the treatment and reuse of wastewater. These technologies should not just aim at treating wastewater for its safe disposal into the environment but also maximizing the recovery of resources from the treatment process. Wastewater is a source of contaminants, such as nutrients, hydrocarbons, heavy metals, endocrine disruptors, microbes, and organic matter, which can have adverse effects on humans and the environment. It can also serve as a breeding ground for disease-causing pathogenic microorganisms such as bacteria, fungi, protozoa, and viruses [7]. Available methods for the treatment of wastewater involve physical, biological, chemical, and mechanical processes such as filtration, precipitation, sedimentation, coagulation/flocculation, oxidation, biodegradation, adsorption, and ion exchange. These processes are costly as they consume a lot of energy and chemicals. The treatment process also generates excess sludge that needs to be disposed of after the treatment. Therefore, there is the need to move towards cheaper and more effective treatment methods [17].

The application of MFCs for treating wastewater offers a more sustainable treatment option and utilization of wastewater as compared to traditional wastewater treatment systems that focus on meeting discharge standards and stabilization of sludge. It has been reported that wastewater has an energy content of 3–10 times higher than the energy required to treat it [23]. With MFC technology, intrinsic energy locked in wastewater in the form of chemicals (such as organic matter and nutritional elements such as nitrogen and phosphorus) and thermal energy can be harvested [23]. Other processes involved in the treatment process that requires electricity can be powered by internally generated energy using this technology. This makes the treatment process energy self-sufficient [23]. Agriculture alone contributes to about 70% of the total freshwater use in the world [3]. Exploring alternative sources of water for the agriculture sector is important as it will reduce the demand for freshwater. Burek et al. [12] projected an annual demand of up to 5,500–6,000 km^3, which translates into about a 20–30% increment above the current water demand level, by the year 2050,

due to rising demands in the industrial and domestic sectors. With wastewater treatment systems providing an alternate source for irrigation water, the stress levels on the demand for freshwater could be reduced. Growth in the agriculture sector would not only ensure food security but would also help mitigate poverty globally. As the production of wastewater is continuous, reclaimed water provides a reliable water source [16]. Using reclaimed water from wastewater treatment for irrigation can help alleviate water scarcity and promote food security. Besides proving an alternative water source for irrigation, reclaimed water can serve as sources of nitrogen and phosphorus needed by plants [16]. Also, it can be a source of plant micronutrients such as iron, manganese, zinc, copper, boron, nickel, and molybdenum. This will help reduce fertilizer needs in crop production [16].

8.5 Energy Production to Reduce Deforestation (SDG 15)

About 2 billion individuals rely on forest goods like natural products, game meat, fibres, and fuelwood to meet basic needs [36]. Fuelwood is a major source of energy for most rural populations across the world. Fuelwood harvesting in developing nations is so significant to the point that it rivals other sources of modern energy like electricity but this is mainly among needy individuals in rustic regions [37].

The utilization of fuelwood, in general, has been identified with deforestation, land debasement, loss of biodiversity, and environmental change [49]. Firewood represents more than 54% of all worldwide gathers per annum which brings about a huge volumes of forest loss [63]. Wood fuels are made of firewood, charcoal, black liquor, and wood waste [18]. It is mostly collected from the forest, often as branches or twigs. The forest constitutes the world's largest and most important terrestrial environment and has the biggest supply of plants and other creatures on land [37]. The demand for sustainable energy is urgent because of the depletion of forest resources, increasing energy consumption, and environmental pollution due to the burning of wood to produce charcoal [48]. Deforestation is the second most significant ozone emissions activity in the world [58]. With the emergence of the MFC technology to produce energy, we can move away from the use of wood fuel and charcoal, which destroy biodiversity.

9 Conclusion

In this chapter, we have discussed the potential benefits of the microbial fuel cell technology to sustainable development through the technology's relevance for the achievement of nine (9) SDGs. The key benefits of the MFC technology identified were wastewater treatment and reuse, energy production, resource recovery, and the prevention of environmental pollution. The MFC technology however requires further research to bring it up to the level of commercialization.

References

1. Abbasi T, Abbasi SA (2011) Decarbonization of fossil fuels as a strategy to control global warming. Renew Sustain Energy Rev 15(4):1828–1834
2. Abdallah L, El-Shennawy T (2013) Reducing carbon dioxide emissions from electricity sector using smart electric grid applications. J Eng 1. https://doi.org/10.1155/2013/845051
3. Abourached C, English MJ, Lui H (2016) Wastewater treatment by microbial fuel cell (MFC) prior irrigation water reuse. J Clean Prod (Elsevier) 137:144. https://doi.org/10.1016/j.jclepro.2016.07.048
4. Adelaja O, Keshavarz T, Kyazze G (2017) Treatment of phenanthrene and benzene using microbial fuel cells operated continuously for possible in situ and ex situ applications. Int Biodeter Biodegrad 116:91–103
5. Aelterman P, Rabaey K, Clauwaert P, Verstraete W (2006) Microbial fuel cells for wastewater treatment. Water Sci Technol. IWA Publishing 54(8):9–15. https://doi.org/10.2166/wst.2006.702
6. Agricultural Waste Management Field Handbook (AWMFH) (2011) Agricultural waste management systems. Agricultural Waste Management Field Handbook. United States Department of Agriculture, pp 4–5
7. Akpor OB, Otohinoyi DA, Olaolu TD, Aderiye BI (2014) Pollutants in wastewater effluents: impacts and remediation processes. Int J Environ Res Earth Sci 3(3):50–51
8. Alhassan EA, Olaoye JO, Olayanju TMA, Okonkwo C.E. (2019). An investigation into some crop residues generation from farming activities and inherent energy potentials in Kwara State, Nigeria. IOP Conf Ser: Mater Sci Eng 640:012093
9. Arun S, Sinharoy A, Pakshirajan K, Lens PNL (2020) Algae based microbial fuel cells for wastewater treatment and recovery of value-added products. Renew Sustain Energy Rev 132:110041
10. Baharudin L, Watson M (2017) Hydrogen applications and research activities in its production routes through catalytic hydrocarbon conversion. Rev Chem Eng 34(1). https://doi.org/10.1515/revce-2016-0040
11. Bose D, Dey A, Banerjee T (2020) Aspects of bioeconomy and microbial fuel cell technologies for sustainable development, vol 13. Mary Ann Liebert Inc., p 3
12. Burek P, Satoh Y, Fischer G, Kahil MT, Scherzer A, Tramberend S, Nava LF, Wada Y, Eisner S, Flörke M, Hanasaki N (2016) Water futures and solution: fast track initiative (final report). In: IIASA working paper. International institute for applied systems analysis (IIASA), Laxenburg, Austria, WP-16-006
13. Cao Y, Mu H, Liu W, Zhang R, Guo J, Xian M, Liu H (2019) Electricigens in the anode of microbial fuel cells: pure cultures versus mixed communities. Microb Cell Factor 18:39
14. Chang IS, Moon H, Jang JK, Kim BH (2005) Improvement of a microbial fuel cell performance as a BOD sensor using respiratory inhibitors. Biosens Bioelectron 20:1856–1859
15. Chaturvedi V, Verma P (2016) Microbial fuel cell: a green approach for the utilization of Waste for the generation of bioelectricity. Bioresour Bioprocess 3(38). https://doi.org/10.1186/s40643-016-0116-6
16. Chen W, Lu S, Jiao W, Wang M, Chang AC (2013) Reclaimed water: a safe irrigation water source? Environ Dev (Elsevier) 8. https://doi.org/10.1016/j.envdev.2013.04.003
17. Crini G, Lichtfouse R (2019) Advantages and disadvantages of techniques used for Wastewater treatment. (Springer Verlag) 17(1):145–155. https://doi.org/10.1007/S10311-018-0785-9
18. Davidsdottir B (2013) Forest products and energy. In: Reference module in earth systems and environmental sciences. Elsevier Inc. https://doi.org/10.1016/B978-0-12-409548-9.01454-8
19. Dermibas A (2006) Global renewable energy resources. In: Energy sources, part A: recovery. Utiliz Environ Effects 28(8):742. https://doi.org/10.1080/00908310600718
20. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells : a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25:464–482. https://doi.org/10.1016/j.biotechadv.2007.05.004

21. Floody DR (2014) Serenity and inner peace: positive perspectives. In: Sims GK, Nelson LL, Puopolo MR (eds) Personal peacefulness: psychological perspectives. Springer Science + Business Media, pp 107–133. https://doi.org/10.1007/978-1-4614-9366-2_5
22. Ghaib K, Ben-Fares F (2018) Power-to-methane. Renew Sustain Energy Rev (Elsevier). https://doi.org/10.1016/j.rser.2017.08.004
23. Gude VG, Kokabian B, Gadhamshetty V (2013) Beneficial bioelectrochemical systems for energy, water, and biomass production. J Microb Biochem Technol 6(5):1–14
24. Hazardous Waste Haulers (HWH) (2021) Hazardous waste statistics to know in 2021. https://hwhenvironmental.com/facts-and-statistics-about-waste/
25. Intergovernmental Panel on Climate Change (IPCC) (2014) Mitigation of climate change. https://www.ipcc.ch/report/ar5/wg3/
26. International Energy Agency (IEA) (2020) Methane tracker 2020. https://www.iea.org/reports/Methane-tracker-2020
27. International Energy Agency (IEA) (2021) Global energy review 2021. IEA, Paris. https://www.iea.org/reports/global-energy-review-2021
28. International Energy Agency (IEA), Nuclear Energy Agency (NEA), Organization for Economic Co operation and Development (OECD) (2015) Projected costs of generating electricity. IEA, NEA and OECD, Paris
29. Jeswani HK, Chilvers A, Azapagic A (2020) Environmental sustainability of biofuels: a review. Proc R Soc A; Math Phys Eng Sci R Soc 476:2243
30. Kokabian B, Gude VG (2015) Sustainable photosynthetic biocathode in microbial desalination cells. Chem Eng J 262:958–965
31. Kondaveeti S, Mohanakrihna G, Lee J, Kalia VC (2019) Methane as a substrate for energy generation using microbial fuel cells. Indian J Microbiol 59(1). https://doi.org/10.1007/s12088-018-0765-6
32. Li X, Wag X, Wan L, Zhang Y, Li N, Li D, Zhou Q (2015) Enhanced biodegradation of aged petroleum hydrocarbons in soils by glucose addition in microbial fuel cells. J Chem Technol Biotechnol 91(1). https://doi.org/10.1002/jctb.4660
33. Liu H, Grot S, Logan BE (2005) Electrochemically assistedmicrobial production of hydrogen from acetate. Environ Sci Technol 4317–20
34. Ma F, Yin Y, Li M (2019) Start-up process modeling of sediment microbial fuel cells based on data driven. Math Probl Eng. https://doi.org/10.1155/2019/7403732
35. Mandal SK, Das N (2018) Application of microbial fuel cells for bioremediation of environmental pollutants: an overview. J Microbiol Biotechnol Food Sci 7(4). https://doi.org/10.15414/jmbfs.2018.7.4.437-444
36. May-Tobin C (2011) Wood for fuel. In: Union of Concerned Scientists, eds. The root of the problem: what's driving tropical deforestation today?
37. Mead DJ, Mead DJ (2005) Forests for energy and the role of planted trees forests for energy and the role of planted trees. Crit Rev Plant Sci 407–421. https://doi.org/10.1080/07352680500316391. Accessed 24 Jan 2015
38. Mohapatra A, Tripathy S (2018) A critical review of the use of fuel cells towards sustainable management of resources. IOP Conf Ser: Mater Sci Eng 377(1):012135. https://doi.org/10.1088/1757-899X/377/1/012135
39. Morris JM, Jin S (2012) Enhanced biodegradation of hydrocarbon-contaminated sediments using microbial fuel cells. J Hazard Mater (Elsevier). /https://doi.org/10.01016/jhazmat.2012.02.09
40. Naik S, Jujjavarapu SE (2021) Self-powered and reusable microbial fuel cell biosensor for Toxicity detection in heavy metal polluted water. J Environ Chem Eng (Elsevier). https://doi.org/10.1016/j.jece.2021.105318
41. Onar OC, Khaligh A (2015) Energy sources. In: Alternative energy in power electronics. Elsevier. https://doi.org/10.1016/B978-0-120416714-8.00002-0
42. Ping Q, Abu-Reesh IM, He Z (2016) Enhanced boron removal by electricity generation in a microbial fuel cell. Desalination 398:165–170

43. Radwan H (2010) Global water resources. Pella Conf Water (1). https://researchgate.net/publication/296488717_Global_Water_resources
44. Saba B (2017) Sustainable power generation from bacterio-algal microbial fuel cells (MFC): an overview. Renew Sustain Energy Rev 73:75–84
45. Sachan VK, Imam SA, Beg MT (2012) Energy-efficient communication methods in wireless sensor networks: a critical review. Int J Comput 39(17). https://doi.org/10.5120/4915-7484
46. Sadh PK, Duhan S, Duhan JS (2018) Agro-industrial wastes and their utilization using solid state fermentation: a review. Bioresour Bioprocess 5:1
47. Salehi H, Burgueno R, Chakrabartty LN, Alavi AH (2021) A comprehensive review of self-powered sensors in civil infrastructure: state-of-the-art and future research trends. Eng Struct (Elsevier) 234. https://doi.org/10.1016/j.engstruct.2021.111963
48. Sandipam S, Velvizhi G (2013) Microbial fuel cells for sustainable bioenergy generation: principles and perspective applications. https://doi.org/10.1007/978-3-642-34519-7
49. Shaheen H, Azad B, Mushtaq A, Waqar R, Khan A (2016) Fuelwood consumption pattern and its impact on forest structure in Kashmir Himalayas Patrón de consumo de leña y sus impactos en la estructura del bosque en Cachemira. Himalaya Bosque 37(2):419–424. https://doi.org/10.4067/S0717-92002016000200020
50. Singla MK, Nijhawan P, Oberoi AS (2021) Hydrogen fuel and fuel cell technology for cleaner future: a review. Environ Sci Pollut Res 28(13). https://doi.org/10.1007/s11356-020-12231-8
51. Song N, Yan Z, Xu H, Yao Z, Wang C, Chen M, Zhao Z, Peng Z, Wang C, Jiang H (2019) Development of a sediment microbial fuel cell-based biosensor for simultaneous online monitoring of dissolved oxygen concentration along depths in lake water. Sci Total Environ 673 (Elsevier). https://doi.org/10.1016/j.scitotenv.2019.04.032
52. Sudirjo E (2020) Plant microbial fuel cell in paddy field: a power source for rural area. Ph.D. thesis. Wageningen University, Wageningen, The Netherlands
53. Sun J, Kingori GP, Si R, Zhai D, Liao Z, Sum D, Zheng T, Yong Y (2015) Microbial fuel cell-based biosensors for environmental monitoring: a review. Water Sci Technol 71(6). https://doi.org/10.2166/wst.2015.035
54. Sun M, Sheng G, Zhang L, Xia C, Mu Z, Liu X, Wang H, Yu H, Qi R, Yu T, Yang M (2008) A MEC-MFC coupled system for biohydrogen production from acetate. Environ Sci Technol 42(21). https://doi.org/10.1021/es801513c
55. Ulrich RS (1984) View through a window may influence recovery from surgery. Science 224(4647). https://doi.org/10.1126/science.6143402
56. United Nations Economic and Social Commission for Asia and the Pacific (UNESCAP) (2001) Introduction types of waste, pp 170–193. https://www.unescap.org/sites/default/files/CH08.PDF
57. Velasquez-Orta SB, Werner D, Varia JC, Mgana S (2017) Microbial fuel cells for inexpensive continuous in-situ monitoring of groundwater quality. Water Res 117 (Elsevier). https://doi.org/10.1016/j.waters.2017.03.040
58. von Witzke H (2008) Agriculture, world food security, bio-energy and climate change: some inconvenient facts. Q J Int Agricult 47(1):1–4
59. Wang G, Huang L, Zhang Y (2008) Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotech Lett 30:1959. https://doi.org/10.1007/s10529-008-9792-4
60. Wang T, Xie H, Chen M, D'Aloia A, Cho J, Wu G, Li Q (2017) Precious metal-free approach to hydrogen electrocatalysis for energy conversion: from mechanism understanding to catalyst design. Nano Energy 42:69–89
61. Wang Y, Lin S, Juang R (2003) Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents 102:291–302. https://doi.org/10.1016/S0304-3894(03)00218-8
62. WCED—World Commission on Environment and Development (1987) Our common future. Oxford University Press, New York. http://www.un-documents.net/our-commonfuture.pdf
63. Williams A, Shackleton CM (2002) Fuel wood use in South Africa: where to in the 21st century? S Afr Forest J 196(1):1–7

64. World Bank (2015) Rising through cities in Ghana: Ghana Uburnization review overview report. The International Bank for Reconstruction and Development/The World Bank. http://documents.worldbank.org/created/en/613252468182958526/pdf/96449-WpPublic-GhanaRisingThroughCities-Overview-full.pdf
65. Yang Z, Tsapekos P, Zhang Y, Zhang Y, Angelidaki I, Wang W (2021) Bio electrochemically extracted nitrogen from residual resources for microbial protein production. Bioresour Technol 337:125353. https://doi.org/10.1016/j.biortech.2021.125353
66. Yang Y, Sun G, Xu M (2011) Microbial fuel cells come of age. Emerg Technol, 625–632. https://doi.org/10.1002/jctb.2570
67. Yaqoob AA, Ibrahim MNM, Umar K, Parveen T, Ahmed A, Lokhat D, Setapar SHM (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214:379–389
68. Yoon J (2013) Introduction to biosensor: from electric circuits to immunosensors. Springer Science & Business Media, USA. https://doi.org/10.1007/978-1-4419-6022-1
69. Zalesny Jr, RS, Stanturf JA, Evett SR, Kandil F, Soriano C (2011) Opportunities for woody crop production using treated wastewater in Egypt. I. Afforestation strategies. Int J Phytoremed 13(sup1):102–121. https://doi.org/10.1080/15226514.2011.568539
70. Zhang F, Tian L, He Z (2011) Powering a wireless temperature sensor using sediment with vertical microbial fuel cells with vertical arrangement of electrodes. J Power Sour 196 (Elsevier). https://doi.org/10.1016/j.jpowsour.2011.07.037

Bioremediation of Organic Pollutants Through Microbial Fuel Cells

Thiruppathi Krithika, Thiruppathi Iswarya, and Thiruppathi Sowndarya

Abstract The microbial fuel cell (MFC) is a bio-electrochemical technique which employs the inherent metabolic characteristics of microorganisms to produce electricity. In the MFC, microorganisms absorb the nutrients within their medium with the release of a portion in the form of electrical energy. MFCs toil as an assuring technology toward renewable power production during the corrosion of biodecomposable organic material in the occurrence of electrogenic bacteria. The accurate application of MFC is synchronous bioremediation and electricity generation. Bioremediation is the method used to manage polluted media, like water, mud, and subsurface matter, through modifying environmental circumstances to incite the growth of microorganisms and diminish the pollutants. Bioremediation becomes accepted generally as a viable choice employing simply resided microorganisms. In these circumstances, MFC could be employed as a possible means to incite bioremediation for the efficient elimination of numerous contaminants. The unique characteristics include energy-saving, not as much sludge, and power generation makes MFCs exceptional technology contrasted to traditional technologies. The chapter is principally directed on the applicability of MFCs towards the elimination of diverse ecological contaminants, viz. antibiotics, pesticides, synthetic dyes, phenol compounds, and polycyclic aromatic hydrocarbons from industrial wastewater. Although the prevailing applicabilities of MFC technology are yet at the lab scales, it will show great prospects for practical applications in the future.

T. Krithika (✉)
PG and Research Department of Microbiology, Hindusthan college of arts & science, Coimbatore 641028, TamilNadu, India
e-mail: krithikat2294@gmail.com; krithlka.t@hlcas.ac.ln

T. Iswarya · T. Sowndarya
Department of Environmetal Sciences, Bharathiar University, Coimbatore 641046, TamilNadu, India

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_10

1 Introduction

The rise in social residents has promoted environmental hazards, directing to the accelerating disintegration of the atmosphere, water, and ground reserves. Wastewater holding numerous pollutants remains the principal cause of environmental pollution in surface and groundwater bodies. But the huge energy expenditure and the operational expense are significant difficulties for the present wastewater management methods, it has been assessed that the processing expense is high almost 3% of the world's electrical power being utilized, as well as sludge dumping expenses, are 50% of wastewater processing [30]. Microbial fuel cells (MFCs) achieved tremendous overall concern in recent years. MFC employs microorganisms for the degradation of organic and inorganic substances beside the production of bioelectrical power [11]. The MFC expertise becomes accepted as it is an eco-friendly strategy contrasted to traditional technologies on the road to the controller of environmental contamination. The major benefits of MFC technology for detoxification of pollutants comprise (i) decreased generation of activated sludge, (ii) gas usage not needed, (iii) energy involvement not necessary for exposure to air, (iv) direct transformation of substrate energy into electricity, and (v) be able to be performed at whichever temperature. In the last 5 years, huge advancements made to improve the enactment of MFCs for both "clean" bio-electricity production and bioremediation of pollutants. Researchers over the world have studied the applicability of MFCs for the processing of various classes of wastewaters from public or household practices, food processing, protein food industrial practice, acidogenic food waste, beverages industry, beer brewery, winery, confectionary industry, dairy industry, yogurt production, agro-processing industry, mustard tuber, cassava mill, palm oil mill, livestock industry, animal carcass, swine, mining and allied industry, recalcitrant pharmaceutical industry, steroidal drug production, paper recycling industry, and petrochemical industries. In this chapter, the applications of MFC towards the bioremediation of the most commonly used organic pollutants are discussed. This chapter is an effort to paraphrase the most current innovative findings on the applicability of MFCs for the bioremediation of organic pollutants. Taken together, this chapter provides insights into the simultaneous wastewater processing and generation of bioelectricity in MFCs.

2 Microbial Fuel Cell and Bioremediation

The MFC is a bio-electrochemical method which employs the normal biochemical reactions of microorganisms particularly bacteria to produce electrical energy. In the MFC, microorganisms use the nutritive substances within their medium and, furthermore, discharge a part of the power reserved in the foodstuff in the state of electricity. MFC comprises an anode compartment and a cathode compartment. These compartments are isolated by the proton exchange membranes (PEM). An MFC's prospective

can be created as the oxidation of organic material by means of bacterial population at the anode chamber along with the reduction of oxygen at the cathode chamber [14]. The advantages of MFC technology in the water purification process are as follows. It transforms pollutants into valuable electrical power during the liberation of CO_2 and H_2O. It guards the inherent ecosystems against environmental deterioration; autonomy of external fuel sources, that tenders it as an energy-proficient technology. It could manage organic and inorganic pollutants, beside high discharge rates. It comprises the production of almost less quantity of sludge. It can further be implemented to manage contaminated soil and gaseous pollutants; hence, soil and air pollution could be overcome especially. It is an environmentally friendly manner since it utilizes ample microbes including air during its functions. Additionally algae, plants, and light can notably enhance the pollutant discharge effectiveness of MFC-based fusion reactors. Algae-based MFC systems can correspondingly be utilized to bring value-added yields from scraps [23]. Rising energy requirements in the current world have created the search for alternate options renewable energy aids and innovative energy generation technologies. MFC technique is recognized as an option that not just generates electrical power but further helps in sewage water management. Conventional fuel cells function based upon electrochemical laws employing hydrogen and oxygen as fuels besides H_2O, high temperature, and electricity as the outputs. Based on the substrates employed in the fuel cell, they are categorized as alkaline fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, solid oxide fuel cells, and polymer electrolyte membrane fuel cells. The peculiar microbial fuel cells employ the usual metabolic reactions of microbes to decompose organic and inorganic substances existing in the sewage water with the simultaneous liberation of protons and electrons. The generated electrons are grasped and used in producing electrical power. According to the discrimination of anodic and cathodic compartments, MFC is categorized as single-chambered MFC and dual-chambered MFC. Among different kinds of wastewater utilized as raw materials, wastewater of food industries, beverage industries, dairy industries, paper recycling industries, and distilleries exhibited the excellent capability to influence MFCs. Animal discard is also employed as a raw substrate in MFCs as its approach is associated with electricity production, as well as electrical power generation. MFCs are standing employed in efficient organic material elimination, metallic elimination, and dye elimination from multifarious classes of wastewater [9].

Employing microbial fuel cells allows an eco-friendly as well as a promising way for transforming organic matter into electricity. MFCs utilize the electrode as a long-term electron receptor for anaerobic microorganisms that improve the decomposition of organic material under anaerobic surroundings. Hence, MFC can degenerate a broad range of organic compounds into biorefractory organics. Recently, remarkable studies converged on evaluating the efficacy of MFC to enhance total carbon removal. Though its by-products are more lethal than the mother compounds in the course of microbial decomposition, accordingly, toxicity subsequent MFC approach necessitates further investigation [26].

3 Bioremediation of Common Organic Pollutants in MFC

The application of microbial fuel cells for the remediation of numerous ecological contaminants such as antibiotics, synthetic dyes, phenolic compounds, polycyclic aromatic hydrocarbons, and pesticides is presented below.

3.1 Bioremediation of Antibiotics

Antibiotics under the most important classes of organic compounds utilized in human and veterinary medicine. They are commonly used worldwide in the animal industry as supplements to enhance animal growth. The use of antibiotics is large and ongoing due to universal economic growth and residents of almost 100,000–200,000 tons/year [35]. Because of improper absorption and lack of biochemical reactions in the intestines of humans and faunas, high antibiotics are released as an unaffected active ingredient and metabolite into feces and urine. Therefore, continued and excessive use of antibiotics causes significant antibiotics occurrence in the environs. Deposits of antibiotics in the atmosphere can be collected by food chains [28].

The problems associated with commonly used antibiotics are their potential side effects in humans. Liver failure, yellow teeth, and stomach problems are caused by the tetracycline antibiotics even in low concentrations. It also causes some allergies in hypersensitive people. In addition, their diet often causes drug intolerance. In particular, antibiotics used to prevent and treat disease are commonly seen in many marine ecosystems. Therefore, the aquatic ecosystem and its associated environmental problems and public health issues continue to pose serious environmental problems [35]. Similarly, appropriate measures to address the problems of antibiotic contamination, especially in animal contaminants, are needed. Sulfonamide (SMs) is one of the most extensively used veterinary classes in the swine industries to prevent diseases that include promoting pig growth. Polluted water in pigs is an example of a major source of bacteria in the atmosphere, due to the large number of antibiotics used in medicine in addition to the feed in the pig industry. SMs are one of the ancient and most broadly used antimicrobial drugs in pig farms in terms of their commercial efficacy and comparability to other common bacterial infections. Recently [6], examined the extraction of large amounts of organic material in pig-contaminated water into a microbial fuel cell and the removal was somehow affected by the availability of SMs. He recommended that a stable voltage be generated at the MFC by supplying the polluted water to the pigs. Adding SMs enhances the generation of electricity by the improved function of exoelectrogenic bacteria following the time of breeding and the improved ability to relocate electrons from the microbe cell to the anode chamber. The concomitant release of sulfamethoxazole, sulfadiazine, and sulfamethazine into microbial fuel cells was significantly stronger than removal from a normal anaerobic reactor.

Zhang et al. [32] reported that the optimal destructive efficiency (>99.29%) of SMX was achieved in the MFC-constructed wetland coupled-biofilm electrode reactor (MFC-CW-BER) system. Cheng et al. [7] used different biochar volumes of pomelo page in the MFC anode chamber and investigated their ability to improve the elimination of SMs in successive MFC operations. The improved effect of adding additional biochar to MFC based on power generation, COD extraction, and nutrient extraction in pig-polluted water was also found. Wen et al. [27] showed that carbon–compound combinations and ratios, external resistance, and aeration length play an important role in regulating sulfamethoxazole and tetracycline elimination and bioelectricity production potential in MFC-CWs (wetlands built with microbial fuel cells). Li et al. [15] tested the efficacy and energy-saving properties of polluted water antibiotics and developed and evaluated an integrated MFC system through granular activated carbon (GAC) expanded by a powerful membrane cathode. Reducing $4e^-$ or $2e^-$ pathway oxidation reactions occur over an extended cathode between GAC or via $FeOOH/TiO_2$/GAC, respectively. Electricity density was pointedly enhanced by another granular activated carbon (GAC), whereas the $2e^-$ pathway ORR produces hydrogen peroxide (H_2O_2) that produces 90% more harmful tetracycline hydrochloride in the forage water. From energy generation awareness and energy ingestion analysis, this integrated MBR/MFC program has been revealed to save energy and is more environmentally approachable than the non-integrated MBR-MFC. The study recommended the use of tiny fuel cells for the effective use of antibiotics.

3.2 Bioremediation of Synthetic Dyes

Dye is a colorful material that is related to the material used. The dye is typically applied to an aqueous solution and necessitates a mordant to progress the speed of the dye mixture in the fiber. Fabric dyes are divided into Azo dye, Nitro dye, Indigo dye, Anthraquinone dye, Phthalein dye, Triphenyl methyl dye, Nitrated dye, etc., based on the chemical structural characteristics [10]. Synthetic dyes are broadly utilized in textile dyeing, paper printing, color photography, medicine, food, cosmetics, and leather industries. About 3,000 types of dye computers are manufactured in the industry and a partial of these dyes belong to the azo dye compounds group. The structure of azo dyes is composed of an amine compound mixed with amine-related or phenol and in addition holds one or more azo bonds (–N=N–). The extraction of these dyes from natural water leads to the reduction of the azo group into fragrant amines and the accumulation of fragrant bio-amines has led to harmful effects on aquatic life as well as carcinogenic and mutagenic effects in humans [24]. Krithika et al. [14] reported a possible mode of action of ligninolytic bacterial consortium in the production of electrical power by the deterioration of the commercially available dyes of azo in a two-chamber MFC. Studies have concluded that ligninolytic bacterial consortium has excellent anti-inflammatory and anti-inflammatory properties. Yadav et al. [29] designed and developed a MFC (CW-MFC) and tested its feasibility. The study confirmed the potential for natural gas production and treatment

of textile wastewater in the CW-MFC. Li et al. [16] developed a MFC and an integrated anaerobic–aerobic detoxification system for the production of simultaneous electrical power generation. Electricity was generated through the process of co-metabolism of glucose and azo dye. The UV–Vis spectra and GC–MS showed that azo linkage was separated by azo dye decolorization under anaerobic conditions in the biological anode compartment and abiotic cathode compartment. Rathour et al. [21] studied eco-electrogenic wastewater treatment of real dyestuff and the expression of small electrode-enriched community structures enriched by Fimbristylisdichotoma implanted in a closed cycle formed by a wetland-MFC (CW-MFC) system. Bakhshian et al. [3] demonstrated the color removal of RB221 (reactive blue 221) using a laccase enzyme in a two-chambered fuel cell. The isolated enzyme of laccase was employed in the cathode compartment without any decolorization mediator of RB221 to enhance the oxygen-reducing response in the cathode. Molasses has been used as an inexpensive and high energy source in the anode compartment. The effect of MFC on synchronous molasses and dye elimination was studied. 87% efficacy of decolorization was succeeded in the cathode compartment and 84% COD elimination of molasses were observed in the anode compartment. Laccase may contribute to the elimination of the reactive blue 221 and have a progressive result on MFC enactment too. High energy density improved by about 30% once enzymatic pigment removal was accomplished in the cathode chamber.

3.3 Bioremediation of Pesticides

Pesticides are persistent organic contaminants that are of attention due to their existence in several ecosystems. Pesticides hold a broad range of synthetic chemical compounds of complex chemical formulations. An increase in the need for agro-products and geographical climate changes resulted in a rise in the utilization and application rate of pesticides [20]. The unrestricted application of pesticides has produced serious environmental and health issues that further affected biodiversity as well. Pesticides are not simply lethal to humans but also pose a warning to the sanctuary of topsoil, aquatic system, and air quality. The pesticide pollution of external and groundwater postures a dangerous menace to the bionetworks. The organochlorine and organophosphates induce tumors, irritability, and convulsions and lead to environmental concerns due to biomagnifications [25].

Generally, pesticides need to be harmful to target insects, and they should not be unintended, including humans. In hindsight, this is also the case with improper pesticide management posing a potential risk to the workplace and environmental hazards. In addition, pesticide residues stored on plants can soon affect public health through food ingestion. The World Health Organization (WHO) summarizes the fact that pesticide poisoning has occurred in one million cases universally and has delivered confirmation that pesticides were liable for cancers that adversely affect various aspects of individual health. Pesticide pollution has contributed to the origins of cancer communities. This term indicates an area where the death degree of cancer is

much more than average, possibly due to pesticide-filled toxins, especially in water [2]. Borello et al. [4] conducted previous research on the use of MFCs to improve DDE (2,2-bis (p-chlorophenyl) -1,1-dichlorethylene) soil pollution. Various laboratory conditions were used to evaluate the performance of MFCs. He reported that MFCs support adequate DDE removal within 2 months. The addition of bulk compost has long-term microbial activity allowed to achieve a percentage of DDE removal in 6 months more than that achieved in 2 months in Soil + DDE MFCs. MFC energy production decreases over time, along with a decreased microbial metabolic activity. P-Nitrophenol (PNP) is used as a contaminant or synthetic intermediary in the preparation of small dyes, pesticides, and drugs. It causes blood disorders and causes renal and hepatic system damage, methemoglobin production, and complete toxicity when severely exposed. Zhao and Kong [33] investigated MFC's ability to lower PNP levels between glucose as the only electron supplier. Its degradation principles were developed using the Box–Behnken experimental design (BBD) combined with a local reaction method (RSM). The effects of PNP degradation were assessed by ultra-performance liquid chromatography quadrupole–time of flight mass spectrometry (UPLC/Q-TOF MS), and a catabolic method was obtained. In addition, the catabolic variability of anodic biofilm in investigated compounds has been explored. The huge effect sequence was used to study the microbiological distribution of biofilm in the MFC anode. Zhao and Zhang [34] examined the release of an electro-Fenton process incorporated into MFCs to release weed-killing mesotrione. Following long-term familiarity, the MFC-Fenton system can detect the effective elimination of mesotrione during microbiological synchronous degeneration and the Fenton oxidation process. The produced bioelectricity is well suited to make H_2O_2 Fenton oxidation at the MFC cathode via 3D modeling. In the meantime, microbiological breakdown and Fenton oxidation have shown degradation variability in many organic compounds. The efficient arrest of microbiological degradation of organic substances at the anode for instantaneous in situ Fenton oxidation at the cathode provides the MFC-Fenton system as a hopeful and continuous treatment for noxious substances.

3.4 Bioremediation of Phenolic Compounds

Phenolic compounds consist of a fragrant compound next to one or more hydroxyl groups mixed with a scented ring. Problems with phenol and its products have attracted international attention. Domestic and industrial activities, such as the production of phenolic resin, the oil industry, the manufacture of pesticides, plastics, cooking, wood products, wood, textiles, baths, detergents, and medicines, remove harmful and deadly phenolic substances from water such as rivers, lakes, and oceans [8].

Phenolic compounds, like catechol, are released from the atmosphere from many industrial sources and present a major ecosystem problem. Too much phenolic, in fact, an anthropogenic source, is considered an important contaminant of water systems. PC toxicity levels are typically between 9 and 25 mg/L in humans and surrounding

aquatic environments, however, harmful effects on biodiversity have been reported even in areas below 1 mg/L. Phenol and some of its products are the most harmful. In humans, they affect severe noxiousness, eye irritation, allergies, and respirational tract and cause skin necrosis. Implantation of skin and weakening of the hepatic system, renal system, and additional interior organs and tissues. They have mutagenic, carcinogenic, neurotoxic, immunotoxic, or endocrine-damaging effects on long-term exposure reported with significant phenolic value. Chlorophenols are one of the principal and utmost abundant sources of phenol-derived substances, especially those found in contaminated water from the chemical, metallurgical, pharmaceutical, pesticide, and textile industries. Plant-causing properties have been stated in various chlorophenols, and substantial amounts have been identified in sipping water, vegetables, and rooster products for public intake. Alkylphenols, like octylphenol ethoxylates and nonylphenol, are a large group of uncharged surfactants, most involved in the construction of industrial scrubbing. These substances reach wastewater purification plants, where they combine with microbiological biotransformation producing various lethal and bio-accumulative metabolites, remarkable for structural simulations of estrogen act as endocrine disruptors in humans and animals. It also damages the CNS and the immune system. International governing bodies have imposed strict limits on phenol extraction and emissions. Both the US Environmental Protection Agency (EPA) and the European Union include several phenolic compounds, especially chlorophenols, nitrophenols, and alkylphenols, in their list of major pollutants in the water policy field [19]. Hedbavna et al. [12] have shown the degradation of biotransformation of phenolic groups of compounds plus their major by-products in groundwater contaminants utilizing bioelectrochemical systems. The phenols were biotransformed anaerobically with 4-hydroxybenzoic acid and 4-hydroxy-3-methyl benzoic acid that were trapped by electro-migration in the anode compartment. Oxygen, nitrate, iron (III), sulfate, and electrode were the receptors for decomposing electrons. Anode-connected electrons generate electricity (~1.8 mW/m^2) while using acetate as an electron supplier. Electricity production began simultaneously along with the reduction of steel; the anode material was an electron receptor as bioenergetically positive as a metal (III). Acetate extraction was increased by 40% in front of the anode compartment. Nonetheless, improved emissions of phenol occur merely for a diminutive time. The limited BES activity of in situ bioremediation necessitates an indulgent of the law and kinetics of reaction involved in the biodegradation of real substances associated with metabolites and the strophic interfaces and carbon sequences in the microbiological population.

3.5 Bioremediation of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are solid impurities with two or more benzene rings. Some are mutagenic, teratogenic, or carcinogenic and can posture a severe hazard to the environs and human wellbeing. The production of PAH is often connected with the unfinished incineration of fuels. Discarded PAHs can hoard

in soil, soil, and sewage [13]. Polycyclic aromatic hydrocarbons have also been found in SHD (Settled House Dust), and several of these composites are known as mutagenic or animal carcinogenic substances. There is a high possibility for human contact to PAHs due to the universal presence of their cradles both indoors plus outdoors which results in inadequate incineration. PAH internal sources comprise gastronomic, heating system, smoldering, wood sweltering, wax light burning, and incense burning. External sources include automotive dissipate, forestry fires, volcanoes, and industrial practices such as melting of aluminum and coke manufacture [18]. The low melting of PAHs creates one of the major problems affecting their efficiency of biodegradation. Due to its long-lasting persistence, immutability, mutagenic and carcinogenic properties, PAHs have received research attention [5]. MFC technology has been formerly studied and conveyed to have biofunctional capability to remediate benzene at the anode. Zhang et al. [31] disputed that benzene bioremediation reconstruction was done by a graphite electrode and the electron received from an impaired sea urchin, signifying the power of electrode-based systems for the destruction of fragrant hydrocarbons in the atmosphere. In the course of simultaneous production of 1000 mg of glucose, he stated that the MFC packing form was used and 600 mg of benzene was completely reduced within 24 h. It is conveyed that the destruction of benzene and power generation occurs simultaneously with potassium ferricyanide substitute as a receptor of electrons. The fragrant benzene ring was probably first analyzed and broken down by mono- and/or dioxygenase, which rises in aerobic or microaerobic surroundings due to the rapid reaction kinetics, benzene can be converted positively under air-conditioned surroundings [1]. In another study, [17] observed and verified the efficacy of sediment microbial fuel cells through modified anode chamber and nanomaterials in in situ bioremediation of polycyclic aromatic hydrocarbons like phenanthrene and pyrene polluted soil. A cost-effective and easy conversion method containing carbon nanomaterials (graphene (GR), graphene oxide (GO), and CNTs (carbon nanotubes)) has been used. Transmitted energy SMFCs, biological concentrations, PHE and PYR in the gut, and the bacterial population at the anode chamber have been inspected.

Sherafatmand and Ng [22] tested sediment microbial fuel cell (SMFC) for polycyclic aromatic hydrocarbons (PAHs) bioremediate in groundwater. The outcomes showed a static power generation of 6.02 ± 0.34 and 3.63 ± 0.37 mW/m^2 under external resistance of 1500 O with aerobic and anaerobic SMFC, respectively. Even though power generation was low, they had low internal resistance (i.e., 436.6 ± 69.4 and 522.1 ± 1.8 O for aerobic and anaerobic SMFC, respectively) compared with collected works. However, the main advantage of this program was its bioremediation capacity, achieving 41.7%, 31.4%, and 36.2% elimination of naphthalene, acenaphthene, and phenanthrene, respectively, in the aerobic environs and 76.9%, 52.5% and 36.8%, respectively, in the anaerobic environment. These results demonstrated the ability of SMFCs in microbial stimulation to replicate the bioremediation of complex and PAH.

4 Conclusion

MFC technology is widely accepted because of its environmentally friendly strategy contrasted to traditional technologies aimed at pollution control. In addition, a number of critics have come together on a variety of concerns linked to MFC technology comprising devices and MFCs configuration, electrode and electrode surface modification, power generation, small statistical analysis, operating conditions and biofilm structure, multiple challenges and opportunities, basic electron transfer mechanisms, biological removal forces, environmental impacts and financial responses regarding the automatic sale of MFCs, etc. However, a complete review of the use of MFCs in pollution control is still lacking. Accordingly, the current chapter aims to compile recent reports on the use of MFCs in emissions from the aquatic ecosystem. MFC technologies may likewise be under attack in future applications in space technology due to their ability to generate energy, sustainable energy production, and the use of biosensors. Although MFCs have been widely used in recent eras, partial achievement has been distinguished in applied performance due to certain boundaries and encounters. Consequently, MFC technology devours so far to receive the attention and attainment of investing in conservational programs.

References

1. Abbas SZ, Rafatullah M, Ismail N, Syakir MI (2017) A review on sediment microbial fuel cells as a new source of sustainable energy and heavy metal remediation: mechanisms and future prospective. Int J Energy Res 41(9):1242–1264. https://doi.org/10.1002/er.3706
2. Alvarez A, Saez JM, Costa JSD, Colin VL, Fuentes MS, Cuozzo SA, Amoroso MJ (2017) Actinobacteria: current research and perspectives for bioremediation of pesticides and heavy metals. Chemosphere 166:41–62. https://doi.org/10.1016/j.chemosphere.2016.09.070
3. Bakhshian S, Kariminia HR, Roshandel R (2011) Bioelectricity generation enhancement in a dual chamber microbial fuel cell under cathodic enzyme catalyzed dye decolorization. Bioresour Technol 102(12):6761–6765
4. Borello D, Gagliardi G, Aimola G, Ancona V, Grenni P, Bagnuolo G, Caracciolo AB (2021) Use of microbial fuel cells for soil remediation: a preliminary study on DDE. Int J Hydrogen Energy 46(16):10131–10142. https://doi.org/10.1016/j.ijhydene.2020.07.074
5. Chebbi A, Hentati D, Zaghden H, Baccar N, Rezgui F, Chalbi M, Chamkha M (2017) Polycyclic aromatic hydrocarbon degradation and biosurfactant production by a newly isolated Pseudomonas sp. strain from used motor oil-contaminated soil. Int Biodeterior Biodegradation 122:128–140. https://doi.org/10.1016/j.ibiod.2017.05.006
6. Chen D, Cheng Y, Zhou N, Chen P, Wang Y, Li K, Ruan R (2020a) Photocatalytic degradation of organic pollutants using TiO_2-based photocatalysts: a review. J Clean Prod 268:121725. https://doi.org/10.1016/j.jclepro.2020.121725
7. Cheng D, Ngo HH, Guo W, Chang SW, Nguyen DD, Li J et al (2020b). Applying a new pomelo peel derived biochar in microbial fell cell for enhancing sulfonamide antibiotics removal in swine wastewater. Bioresour Technol 318:123886. https://doi.org/10.1016/j.biortech.2020.123886
8. Cheng D, Ngo HH, Guo W, Lee D, Nghiem DL, Zhang J, Wang J (2020c) Performance of microbial fuel cell for treating swine wastewater containing sulfonamide antibiotics. Bioresour Technol 311:123588. https://doi.org/10.1016/j.biortech.2020.123588

9. Choudhury P, Ray RN, Bandyopadhyay TK, Basak B, Muthuraj M, Bhunia B (2021) Process engineering for stable power recovery from dairy wastewater using microbial fuel cell. Int J Hydrog Energy 46(4):3171–3182. https://doi.org/10.1016/j.ijhydene.2020.06.152
10. El Harfi S, El Harfi A (2017) Classifications, properties and applications of textile dyes: a review. Appl J Environ Eng Sci 3(3);00000-3. https://doi.org/10.48422/IMIST.PRSM/ajees-v3i3.9681
11. He CS, Mu ZX, Yang HY, Wang YZ, Mu Y, Yu HQ (2015) Electron acceptors for energy generation in microbial fuel cells fed with wastewaters: a mini-review. Chemosphere 140:12–17. https://doi.org/10.1016/j.chemosphere.2015.03.059
12. Hedbavna P, Rolfe SA, Huang WE, Thornton SF (2016) Biodegradation of phenolic compounds and their metabolites in contaminated groundwater using microbial fuel cells. Biores Technol 200:426–434. https://doi.org/10.1016/j.biortech.2015.09.092
13. Košnář Z, Wiesnerová L, Částková T, Kroulíková S, Bouček J, Mercl F, Tlustoš P (2019) Bioremediation of polycyclic aromatic hydrocarbons (PAHs) present in biomass fly ash by co-composting and co-vermicomposting. J Hazard Mater 369:79–86. https://doi.org/10.1016/j.jhazmat.2019.02.037
14. Krithika T, Kavitha R, Dinesh M, Angayarkanni J (2021) Assessment of ligninolytic bacterial consortium for the degradation of azo dye with electricity generation in a dual-chambered microbial fuel cell. Environ Challenge 4:100093. https://doi.org/10.1016/j.envc.2021.100093
15. Li Y, Liu L, Yang F (2017) Destruction of tetracycline hydrochloride antibiotics by FeOOH/TiO_2 granular activated carbon as expanded cathode in low-cost MBR/MFC coupled system. J Membr Sci 525:202–209. https://doi.org/10.1016/j.memsci.2016.10.047
16. Li Z, Zhang X, Lin J, Han S, Lei L (2010) Azo dye treatment with simultaneous electricity production in an anaerobic–aerobic sequential reactor and microbial fuel cell coupled system. Biores Technol 101(12):4440–4445. https://doi.org/10.1016/j.biortech.2010.01.114
17. Liang Y, Zhai H, Liu B, Ji M, Li J (2020) Carbon nanomaterial-modified graphite felt as an anode enhanced the power production and polycyclic aromatic hydrocarbon removal in sediment microbial fuel cells. Sci Total Environ 713:136483. https://doi.org/10.1016/j.scitotenv.2019.136483
18. Maertens RM, Yang X, Zhu J, Gagne RW, Douglas GR, White PA (2008) Mutagenic and carcinogenic hazards of settled house dust I: polycyclic aromatic hydrocarbon content and excess lifetime cancer risk from preschool exposure. Environ Sci Technol 42(5):1747–1753. https://doi.org/10.1021/es702449cCCC
19. Maza-Márquez P, González-Martínez A, Juárez-Jiménez B, Rodelas B, González-López J (2018) Microalgae-bacteria consortia for the removal of phenolic compounds from industrial wastewaters. In: Approaches in bioremediation. Springer, Cham, pp 135–184. https://doi.org/10.1007/978-3-030-02369-0_8
20. Odukkathil G, Vasudevan N (2013) Toxicity and bioremediation of pesticides in agricultural soil. Rev Environ Sci Bio/Technol 12(4):421–444. https://doi.org/10.1007/s11157-013-9320-4
21. Rathour R, Patel D, Shaikh S, Desai C (2019) Eco-electrogenic treatment of dyestuff wastewater using constructed wetland-microbial fuel cell system with an evaluation of electrode-enriched microbial community structures. Bioresour Technol 285:121349. https://doi.org/10.1016/j.biortech.2019.121349
22. Sherafatmand M, Ng HY (2015) Using sediment microbial fuel cells (SMFCs) for bioremediation of polycyclic aromatic hydrocarbons (PAHs). Biores Technol 195:122–130. https://doi.org/10.1016/j.biortech.2015.06.002
23. Suresh R, Rajendran S, Kumar PS, Dutta K, Vo DVN (2022) Current advances in microbial fuel cell technology toward removal of organic contaminants—A review. Chemosphere 287:132186
24. Thiruppathi K, Rangasamy K, Ramasamy M, Muthu D (2021) Evaluation of textile dye degrading potential of ligninolytic bacterial consortia. Environ Challenge 4:100078. https://doi.org/10.1016/j.envc.2021.100078
25. Uqab B, Mudasir S, Nazir R (2016) Review on bioremediation of pesticides. J Bioremed Biodegrad 7(343):2. https://doi.org/10.4172/2155-6199.1000343

26. Wang J, He MF, Zhang D, Ren Z, Song TS, Xie J (2017) Simultaneous degradation of tetracycline by a microbial fuel cell and its toxicity evaluation by zebrafish. RSC Adv 7(70):44226–44233. https://doi.org/10.1039/c7ra07799h
27. Wen H, Zhu H, Xu Y, Yan B, Shutes B, Bañuelos G, Wang X (2021) Removal of sulfamethoxazole and tetracycline in constructed wetlands integrated with microbial fuel cells influenced by influent and operational conditions. Environ Pollut 272:115988. https://doi.org/10.1016/j.envpol.2020.115988
28. Wen H, Zhu H, Yan B, Xu Y, Shutes B (2020) Treatment of typical antibiotics in constructed wetlands integrated with microbial fuel cells: roles of plant and circuit operation mode. Chemosphere 250:126252. https://doi.org/10.1016/j.chemosphere.2020.126252
29. Yadav AK, Dash P, Mohanty A, Abbassi R, Mishra BK (2012) Performance assessment of innovative constructed wetland-microbial fuel cell for electricity production and dye removal. Ecol Eng 47:126–131. https://doi.org/10.1016/j.ecoleng.2012.06.029
30. Ye Y, Ngo HH, Guo W, Chang SW, Nguyen DD, Liu Y, Ni BJ, Zhang X (2019) Microbial fuel cell for nutrient recovery and electricity generation from municipal wastewater under different ammonium concentrations. BioresourTechnol 292:121992. https://doi.org/10.1016/j.biortech.2019.121992
31. Zhang T, Gannon SM, Nevin KP, Franks AE, Lovley DR (2010) Stimulating the anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. Environ Microbiol 12(4):1011–1020. https://doi.org/10.1111/j.1462-2920.2009.02145.x
32. Zhang S, Song HL, Yang XL, Li H, Wang YW (2018) A system composed of a biofilm electrode reactor and a microbial fuel cell-constructed wetland exhibited efficient sulfamethoxazole removal but induced sul genes. Biores Technol 256:224–231. https://doi.org/10.1016/j.biortech.2018.02.023
33. Zhao H, Kong CH (2018) Enhanced removal of p-nitrophenol in a microbial fuel cell after long-term operation and the catabolic versatility of its microbial community. Chem Eng J 339:424–431. https://doi.org/10.1016/j.cej.2018.01.158
34. Zhao H, Zhang Q (2021) Performance of electro-Fenton process coupling with microbial fuel cell for simultaneous removal of herbicide mesotrione. Bioresour Technol 319:124244. https://doi.org/10.1016/j.biortech.2020.124244
35. Zhou Y, Zhu N, Guo W, Wang Y, Huang X, Wu P, Xian J (2018) Simultaneous electricity production and antibiotics removal by microbial fuel cells. J Environ Manag 217:565–572. https://doi.org/10.1016/j.jenvman.2018.04.013

Bioremediation of Pharmaceutical Pollutants Through Microbial Fuel Cells

Lali Growther, V. Mahalakshmi, and P. Yoonus

Abstract Industrial revolution though has a positive impact on production, has resulted in a wide range of pollutants, which are discharged as landfills or into the aquatic ecosystems without prior treatment thereby polluting the environment. Biomedical wastes, especially pharmaceutical wastes are of great concern. Pollutants like antibiotics, antipyretic elements, analgesics, antidepressants, antihypertensive, contraceptives, steroids, hormones, drugs, and chemical residues from pharmaceutical industries are labeled as environmental hazards that may cause a grave menace to human life and the ecosystem at large. Antibiotics are a major source of concern as these antibiotics will pave the way for developing antimicrobial resistance and transfer resistance to other populations of microorganisms. Other organic and inorganic pollutants include hazardous chemicals that need to be treated before disposal into the environment. There are several technologies and methodologies that are being used by scientists and environmentalists to reduce these toxic effects. Microorganisms play a significant part in bioremediation. The most promising technology that is emerging and eco-friendly is the use of microbial fuel cells (MFCs). This system operates with microbial populations or consortia in the degradation of pollutants and generating electric current simultaneously. This review highlights the toxic pollutants from pharmaceutical industries, sources of entry of these chemicals into the environment, their toxicity, health risk, and the possible ways of bioremediating these pollutants. It is crystal clear from the available literary writings on MFCs that they have shown tremendous potential in the removal of various pollutants. This technology uses microorganisms to degrade toxic bioactive pollutants to non-toxic forms with the generation of electricity. This is an eco-friendly technology for a sustainable future.

L. Growther (✉) · P. Yoonus
Department of Microbiology, Hindusthan College of Arts & Science, Coimbatore, India
e-mail: lallgrowther@hlcas.ac.ln

P. Yoonus
e-mail: yoonuspth@gmall.com

V. Mahalakshmi
Department of Microbiology, Madras Christian College, Chennai, India
e-mail: mahalakshml@mcc.edu.ln

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_11

Keywords Pharmaceutical wastes · Bioremediation · Pollutants · Microbial fuel cells · Antibiotic resistance

1 Introduction

Nearly 50% of the demand for vaccines globally is met by the Indian Pharmaceutical Industry and hence India is considered to be the largest provider of generic drugs in the global market. Since pharmaceutical industries, manufacture lifesaving medicines, they are given prime importance. Apart from this, toxic pollutants are also generated that cause a grave menace to the environment, by reducing the quality of water, thereby harming the health of mankind. Therefore, the pharmaceutical industry has become a center of great concern. With the increasing demand for water, reuse of treated pharmaceutical wastewater using economic, safe, and sustainable treatment methods is required. The contamination of the environment by heavy metals and synthetic xenobiotics became a huge threat after Industrialization. Several pollutants pollute the groundwater, to name a few are pharmaceutical compounds, petroleum products, chloro- and nitrophenols and their derivatives, polycyclic aromatic hydrocarbons, organic dyes, and pesticides. Due to the developments in medical research, there is a tremendous increase in the production of a large number of drugs and other medically important items. But on the other side of the coin, these pharmaceutical industries have also added many compounds to the environment, thus polluting it. Chang et al. in the year 2008 have reported that the effluent generated from the pharmaceutical industries, which contains the raw materials used during the production of antimicrobials, multifarious drugs, and toiletries, will in sequence harm humans and aquatic life. These compounds may induce mutation because of their carcinogenic and genotoxic nature [1].

2 Need for Pharmaceutical Industries

The pharmaceutical industry in the pandemic era is expected to come out with new medicines including vaccines, antineoplastics, and chemotherapeutic agents. In order to combat multifarious combinations of illnesses and diseases, these industries have started investing in innovation and futuristic ideations. But this method of investment may involve huge risk because for every thousand of new compounds tested, only a negligible number of compounds may reach the next stage, i.e., animal testing, very few may reach human clinical trials and, finally, one compound will be approved for sale in the marketplace, as per the guidelines of the regulatory authorities [2]. Keeping this in mind, recent research should invest in developing an innovative medical instrument that may require limited antibiotics for treating infectious diseases. This has enabled the pharmaceutical industry to move towards the

development of novel production systems, processes, and products that are sustainable. The obligatory personal care requirements are the use of innovative therapies, biopolymers as packaging materials, and medicines/drugs with prolonged efficacy and/or safety in previously treatable diseases. However, pharmaceutical pollutants are of major concern. Traces of chemicals in different forms pollute the soil and water in many ways. Hence, the high point is the need of a persistent connection linking R&D on real-time evaluation and care of cropping up contaminants and the instrument involved in the processes. This kind of an integrated approach should analyze the shelf life of the contaminants commencing from the origin to discharge to their elimination via bioremediation techniques, in addition also the health risks of these pollutants during this transmission process.

3 Pharmaceutical Pollutants

Pharmaceutical wastes can be solid or liquid. The nature of the waste is varied, complex, and recalcitrant. This is a kind of biomedical waste. In India, about 50–60% of the total solid waste generated is biomedical waste. The public law entitled "Resource Conservation and Recovery Act" (RCRA) provides us with the design for the proper handling of unsafe and non-hazardous solid wastes. The RCRA, based on the unique characteristics of hazardous wastes has categorized them into decisive lists of chemicals.

4 Solid Pharmaceutical Waste

Solid pharmaceutical waste is of a great concern because it contains both plastic and metals. It comprises mostly of used pharmaceutical residues like scalpels, needles, catheters, saline bottles, saline nasal sprays and syringes, contaminated items like blood/pus stained bandages, gloves, masks, and intravenous bags and tubing, drugs distribution devices like autoinjectors, inhalers and nebulizers, bare cases of drug containers, bubble cards, liquor therapeutics, and lotion. The regulations for the disposal of pharmaceutical wastes in accordance with the notification from the Ministry of Environment, Forest (MoEF) and Climate change, Government of India, published in the year 2016, (on 28 March) in the Gazette of India, New Delhi, under Part II, Sect. 3, Sub-section (i), stresses the usage of non-chlorinated plastic bags, which are yellow-colored, or containers for the discarding of antimicrobials, antileukemic medicines, and things polluted with antileukemic medicines such as hermetically sealed containers made of glass and plastics. However, run out antileukemic medicines have to be eliminated by incineration at temperature >1200 °C, either through producer or distributer fretwork. This incineration can also

happen in a customary infectious waste treatment facility or a compost facility (at >1200 °C) Or encapsulation or plasma pyrolysis at >1200 °C. Similarly, other scrap drugs also can be disposed by incineration.

5 Liquid Pharmaceutical Waste

Pharmaceutical manufacturing facilities, performing process operations, usually release huge volumes of liquid wastes such as slurry from chemical processing and taint solvents after cleaning tanks. Cecconet et al., in the year 2017, reported that liquid pharmaceutical wastes are the result of two opposed origins, the first being the pharmaceutical manufacturing units and the second from the day-to-day usage of pharmaceuticals. In addition, the Wastewater Treatment Plants (WWTPs) that are not accurately planned for the discarding of pharmaceutically active compounds (PhACs) may also act as the main reason for liquid pharmaceutical wastes. [3]. According to [4–6], the effluent from pharmaceutical industry may have a high level of pollutants including non-biodegradable organic matter such as antibiotics, other prescription drugs, non-prescription drugs, animal and plant steroids, reproductive hormones, beta-lactamides, anti-inflammatories, analgesics, lipid regulators, anti-depressants, cytostatic agents, personal care products, detergent metabolites, flame retardants, products of oil use and combustion, and other extensively used chemicals, i.e., spent solvents, reaction residues, used filter media, etc., and heavy metals such as lead, mercury, cadmium, nickel, chromium, etc.

6 Listed Hazardous Chemicals in Pharmaceutical Waste and Their Health Impact

The RCRA lists of hazardous wastes comprise various pharmaceutical wastes and, in addition, these lists categorize a number of these wastes as acute hazardous pharmaceutical waste. Even a trace of acutely hazardous waste is toxic to the environment. The four main characteristics of hazardous wastes as listed by the Environmental Protection Agency (EPA) are their explosive reactive, toxic nature, and corrosiveness. Different letters of alphabets are being used to distinguish these wastes based on their characteristics and RCRA has made use of the alphabets F, K, P, and U to list wastes. A commercial chemical product is designated as P by EPA and the U-list resolves that the chemical is either cent percent pure, scientific, or the sole component in formulating a chemical. Thus, the P-list and the U-list help in identifying severe and dangerous wastes from rejected chemicals used in business, and this list is found at 40, The Code of Federal Regulations (CFR) under section 261.33.

Some of hazardous pharmaceuticals (at concentrations of more than 0.3%) identified by the P-list are arsenic trioxide, epinephrine, nicotine, phentermine, physostigmine, physostigimine salicylate, and warfarin. The sample hazardous pharmaceuticals in the U-list are chemotherapy drugs like cyclophosphamide, daunomycin, melphalan, streptozotocin, and Diethylstilbestrol (DES), the chemical responsible for severe birth defects also finds a place in the U-list. However, the F-listed wastes mostly include solvents used in protocols followed in diagnostic laboratories. Spent non-halogenated solvents like xylene, acetone, ethyl acetate, N-butyl alcohol, cyclohexanone, methanol, toluene, isobutanol, benzene, etc., are the best examples of hazardous compounds in F-list. On the other hand, the K-list pinpoints the dangerous wastes from manufacturing (also veterinary pharmaceuticals manufacturing) and industrial sectors. The slurry from wastewater treatment units of the production units of veterinary pharmaceuticals containing arsenic or oregano arsenic compounds finds a place under hazardous chemicals on the K-list.

7 Sources of Pharmaceutical Wastes in the Environment

Many are the entry points of these pharmaceutical wastes into the environment. It includes improper disposal of unused as well as expired medicines from household into the dustbins that gets collected through the municipal waste collection systems or directly into the soil and water systems. After consumption, medicines are excreted in urine or feces of humans or animals. Only a portion of the active component is metabolized, and the remaining is excreted. Pharmaceutical Industries themselves are another source. Hospital biomedical waste is yet another source. Veterinary, dairy, release from aquaculture, farming, and pest control also are major sources. According to [7], open water resources are the usual sites of wastewater disposal by industries. Powerful antibiotics have been determined in the water supplies at agglomerations that harm plants and algae, thus threatening the aquatic ecosystems. The act of directly disposing of the physician samples provided by companies to medical representatives for the purpose of sale promotion is prevalent in India and many developing countries. Often, we hear news about expired/unused drug products being dumped across roadside. Kadam et al., in the year 2016, reported that in India, as per the data published by the Central Pollution Control Board, nearly 4,057 tonnes of waste/day are generated by registered healthcare facilities. Another data had estimated that every year, 100,000 tons of antimicrobials are consumed [8]. Therefore, efforts need to be taken to lessen pharmaceutical waste production, thereby conserving precious resources and simultaneously safeguarding the environment. Also, care needs to be taken that slowly degradable and recalcitrant pollutants do not enter the environment for they present a serious risk for they persist, or get disseminated in the environment, resulting in biomagnification. Hence, these substances are labeled as Environmentally Persistent Pharmaceutical Pollutants (EPPPs). Arsenic trioxide is a heavy metal that causes serious health effects on exposure. It is used to treat cancer. It binds to sulfhydryl groups of proteins and inhibits energy production.

However, it has been reported to cause death due to multiple organ failure. Symptoms include nausea, vomiting, and diarrhea. Other effects of long-time exposures are cerebral edema, cardiotoxicity, lung cancer, and cancers of skin, liver, bladder, and kidneys.

8 Possible Ways of Bioremediating Pharmaceutical Pollutants

The form and chemical reactions of pharmaceutical pollutants have been reviewed by [9]. The physical and chemical remediation methods, which are presently used include coagulation/flocculation, hydrolysis, photocatalysis, filtration, and advanced oxidation processes by application of ozone, hydrogen peroxide, and ultraviolet light, though not applicable often, may be exorbitant resulting in secondary pollution. The characteristics of the pollutants are to be reviewed to decide their fate and behavior in the environment and simultaneously modernize the option of bioremediation strategy for effective monitoring and managing the pollutants. Due to the availability of insufficient information, it is difficult to presume that trace amounts of chemicals/pollutants could be minimized or removed from the environment. It is becoming obvious that there is a demand for cost-effective and structured remediation technologies such as bioremediation, because of the huge determination of pharmaceuticals wastes and their by-products in the surroundings. With a fixed activated sludge process of treating wastewater, pollution control is feasible in aquatic ecosystems. But bioremediation using the traditional treatment systems, such as activated sludge conveyed less competency in eliminating Endocrine-Disrupting Compounds (EDCs) from wastewater; even multiple treatment systems using WWTP proved inefficient [10]. Under this circumstance, Membrane Bioreactors (MBRs) or fluidized bed bioreactors are considered to attainable choice in proportion to traditional treatment plants for they are effective in moving obstinate substances, which are difficult to be eliminated or degraded by biological means in activated sludge systems [11, 12]. In addition, white rot fungi and their oxidative enzymes are also found to be potential candidates in bioremediating wastewaters containing EDCs and bisphenol A, the ever-present plasticizer [13, 14].

9 Bioremediation

Microbial ability to degrade chemical compounds has been extensively used today. Many studies reported that microorganisms are able to degrade various pollutants. Microorganisms use industrial crude pollutants as sources of energy and carbon. Microbes can break down organic pollutants by their metabolic processes or by cometabolism. Bioremediation is the process of degradation of toxic pollutants using

microbial consortium. This process is economically viable and eco-friendly. This prevents seepage of these toxic pollutants into the groundwater. Even though some toxic compounds are produced during degradation of certain pollutants, the process provides an enduring solution as it may result in the transformation of pollutants into non-detrimental or less toxic compounds. Biodegradation properties can be employed as different techniques. These techniques include coagulation, precipitation or flocculation, filtration or sedimentation, adsorption, fluoridation, membrane bioreactor, electrochemical treatments, and immobilization. Several researches have been carried out on using individual microorganisms and consortiums to degrade harmful pollutants from the environment and different techniques to enhance the rate of bioremediation [15].

10 Microbial Fuel Cells

The use of microorganisms to generate electrical energy is called microbial fuel cells (MFCs). This tool uses microorganisms to convert the chemical energy in organic substrates into electrical energy. This mechanism to generate electricity using microbes was first invented by [16]. To generate electricity, Potter used *Saccharomyces cerevisiae* in the laboratory [17]. This eco-friendly device offers a twofold advantage like the generation of bioelectricity and waste management. In a MFC, the proton exchange chamber separates the two chambers. One chamber is for anode and another is for cathode. Materials used for making electrodes are different in various MFCs. The electrodes frequently used in MFCs are carbon-containing resources. These materials are generally used because of their chemical stability, commendable electrical conductivity, low price, biocompatibility, and non-corrosiveness; on the other hand, they show less electrocatalytic activity for microbial growth [18]. When degradation of organic compounds occurs by microbes, electrons are released. These electrons are passed to the cathode through an electric circuit. Bacteria with this ability are called "Exoelectrogens" (Exo-refers to extracellular; "electrogens" refers to the ability of transferring electrons directly to an element). At the cathode, electrons reach through the external circuit, and hydrogen ions shift to the cathode reacting with oxygen, forming water in the internal circuit. The particular features together with less sludge, power-saving, and energy creation make this technology using microorganisms an exceptional technology when compared to the traditional technologies (Sanjeeb Kumar Mandal and Nilanjana Das, 2018). As microorganisms are in abundance in nature, electricity production in this way is cheaper to a greater extent with nearly zero carbon emission as reported by Zhou et al. [19]. Thus, this technology of using MFCs shows a prospective approach to generate green "electricity." [20]. Nevertheless, several factors like electrode spacing, internal resistance, substrates, electrode material properties, catalyst, and ion concentration play a major role in the output of electricity through these fuel cells [21]. An important factor to make MFCs productive as well as competent at the industrial level is the material used in electrode. Bioremediation can be made feasible with the application

of MFCs. Although the outcomes of using MFCs in bioremediation show remarkable results, future research is warranted on the bioremediation of environmental pollutants [22–24].

11 Microbial Fuel Cells and Bioremediation Using Bacteria

Promising results are seen in the removal of organic contaminants, recovery of possible energy from wastewaters, and other toxic pollutants of interest at the laboratory-scale studies. Generation of electricity and the efficacy of pollutant removal are the major properties to check the performance of an MFC. The product of voltage and current is measured as the power generated. Information on the efficacy of pollutant removal can be measured by the difference in the chemical oxygen demand (COD) value between the influent and effluent [25]. The following table shows the bacteria used in bioremediation of pharmaceutical wastes like benzene, triclosan, and phenanthrene using bacteria and the yield (Table 1).

12 Microbial Fuel Cells and Bioremediation Using Microalgae

Microalgae also have a beneficial role as a MFC. Microalgae like *Spirulina platensis*, *Chlamydomaonas reinhardtic,* Synechococcus sp., Chlorococcum sp., *Chlorella pyrenoidosa., Laminaria saccharina,* and other algae are being studied. According to [28], generation of electricity both in light and dark conditions by *Spirulina platensis* was studied. This alga produced a power of 1.64 $mWm^{-2}1$ under dark conditions. The yield obtained is ten times higher when *Spirulina* is used in dark conditions than in day conditions [29]. Similar to photosynthesis, the intensity of light also is a factor that affects the efficacy of power density and electricity production. Many researchers have studied another species of algae, the Chlorella sp. [30] used different algae and rock phosphate as a substrate. They recorded higher algal biomass as well as energy yield. Apart from these factors, batch and continuous modes of cultivation also play a significant role. In case of Chlorella, continuous cultivation had shown higher energy yield. When an abiotic MFC is fed with microalgae [31], has obtained 128 μW power and biomass. However, [32] produced different bio-energies using several photobioreactors (PBR) collectively in tanks with the microalgae *Chlorella vulgaris.* The impact of a range of light intensities from 100 to 900 lx, was studied using *Chlamydomaonas reinhardtic* on photo microbial fuel cells (PMFC) [33]. Enhanced efficacy of photosynthetic microbial fuel cells was found at higher light intensity. The supreme benefit by means of live microalgae is that they simultaneously produce biomass and are a storehouse of O_2. This biomass is a stock of single-cell proteins, nutrient supplements, and biofuel [34]. Regardless of the fact that several microorganisms

Table 1 Types of Pharmaceutical waste, bacteria used, and the yield of electricity

Sl.No	Type of pharma waste	Type of MFC	Organism used (Bacteria)	Electrode used—anode/cathode	Yield of electricity	References
1.	Benzene	Dual-chamber Benthic microbial fuel cell (BMFC) reactor made of plexiglass bottles	*Pseudomonas* sp. and *Bacillus* sp.	cylindrical graphite rods	24.2 mW/m^2	Umar et al. [26]
2.	Triclosan	Microbial fuel cells (3 chambered) divided by a cation exchange membrane	*Geothrix, Corynebacterium, Sulfobacillus, GOUTA19, Geobacter, Acidithiobacillus,* and *Acinetobacter*	Carbon felt (9 × 9 cm^2, 1 cm thick) linked with a titanium wire	420 ± 50 mV	Wang Lu et al. [25]
3.	Phenanthrene	Dual-chamber MFC made of glass bottles separated with cationic exchange membrane	*Shewanella oneidensis* (MR1 14,063) and *Pseudomonas aeruginosa* (NCTC 10,662 *Pseudomonas aeruginosa Schewanella oneidensis*	Carbon felt (4.0 cm × 5.0 cm)	1.11 ± 0.07 mW/m^2	Adelaja et al. [27]

Table 2 Microalgae used MFC and their power outputs

Sl.No	Organism used (Algae)	Power density (Wm^{-2})	References
1.	*Chlorella pyrenoidosa*	0.0302	Liu et al. [38]
2.	*Chlamydomonas* sp.	0.075	Nishio et al. [39]
3.	*Scenedesmus obliqus*	0.102	Khandelwal et al. [30]
4.	*Chlorella vulgaris*	0.187	Liu et al. [38]
5.	*Laminaria saccharina*	0.25	Vinayak et al. [35]
6.	*Spirulina platensis*	0.0065	Fu et al. [40]
7.	*Dunaliella* sp.	0.0053	Lakaniemi et al. [41]
8.	Synechococcus sp.	0.0956	Mohamed et al. [37]
9.	Chlorococcum sp.	0.0302	Mohamed et al. [37]
10.	*Microcystis aeruginosa*	0.0830	Vinayak et al. [35]
11.	Synechococcus sp.	0.0956	Lakshmidevi et al. [42]
12.	Chlorella sp.	0.0033	Elakkiya and Niju [43]
13.	Chlorella sp.	0.0197	Abazarian et al. [44]
14.	*Chlorella vulgaris*	0.089	Khandelwal et al. [30]
15.	*Chlorella vulgaris*	0.3720	Zhang et al. [45, 46]

are present in wastewater, their ability to remediate toxic pollutants in wastewater by producing electricity is not always environmental-friendly and simple to use. For this reason, using microalgae is advantageous and a good replacement at anode, because, in addition to having excellent growth in wastewater, they can produce value-added products and electricity. Recycling of wastewaters with high concentrations of nitrates, phosphates, and other organic carbon sources for industrial applications is possible with microalgae-based MFCs [35]. Microalgae-based MFCs and their energy outputs are tabulated (Table 2).

In an MFC, (with algae) with diverse groups of microbes like *Dunaliella tertiolecta, Chlorella vulgaris,* Chlorococcum sp., *Microcystis aeruginosa,* and Synechococcus sp., it was found that the highest Power Density (MPD) of 30.2 ± 0.8 mWm^{-2} while using Chlorococcum sp. and 41.5 ± 1.2 mW^{-2} while using the algae Synechococcus sp. [36, 37].

Therefore, more investigations on MFCs and their coupled expertise are essential to produce electricity at the commercial scale. MFCs conservatively make use of bacteria to act as biobatteries. However, a lot of catalyst and coupling agents which utilize microbes like bacteria and/or green algae along with semiconductors have given a new era of photoelectric and photocatalytic fuel cells. Nevertheless, microalgae like diatoms in an MFC together with PMFC/Photoelectrocatalytic would in near future, will not only be used for Diafuel™ (Biofuel from Diatoms) production but also to run hybrid electric vehicles using bioelectricity [47, 48]. This technology can also be used for extraction of primary and secondary metabolites at the same time to produce value-added products from microalgae and bacteria at a cost-effective scale. To accomplish this, it is important to reduce the cost of production and increase

the yield at the manufacturing level. This area necessitates more research to formulate it to the industrial level for meeting the demands globally. Even though a lot of research on various pollutants and their bioremediation has been done to a greater extent and much is talked about MFCs, with the huge wealth of so many microalgal species in the oceans, still, many of them are novel, unexplored, and untested for their use in MFCs [35, 49].

13 Antibiotics and Microbial Fuel Cells

MFCs are gaining popularity as a viable method for bioremediation of pharmaceuticals, which are a huge concern to humanity. According to Hong Song et al., metronidazole elimination in MFCs was 85.4% within 24 h, while only 35.2% was accomplished in open circuits. Antibiotics like metronidazole, according to the findings, might be eliminated from MFCs. The greater degradation and mineralization rates are 95% and 90%, respectively, mg/L/h. In the presence of 10 mg/L Fe(III) and an incoming photon flux of 23.3 mW/cm^2, power output of 251 mW/m^2 was achieved at a Mo/W ratio of 0.17: 1.0 with Mo/W loading of 0.18 mg/cm^2 [50]. Chloramphenicol is a hazardous antibiotic with a broad spectrum of action that has been outlawed in developed countries but is still used in underdeveloped ones. Zhang et al. [51] investigated the efficiency of a MFC for chloramphenicol degradation, finding that the MFC degraded 84% of 50 mg/L Chloramphenicol in about 12 h. Lu [52], demonstrated another rapid breakdown (85% after 12 h) of the broad-range antibiotic sulfamethoxazole (SMX) utilizing an MFC. They found that microbes in fuel cells possess almost three times higher level of ATP than that of open-circuit controls, which could explain why SMX in MFCs degrades so quickly. Paracetamol, a common painkiller and sedative, is another big contaminant. The bioelectrochemical breakdown of paracetamol in an MFC–Fenton system was investigated by Baogang [53]. MFC reactors with two chambers were employed. For bio-electrochemical paracetamol degradation, Fenton reactions were used to MFCs without input of external power. At a starting pH of 2.0, 20 X external resistance, and a 5 mg/L concentration of iron, the maximum degradation efficiency of 70% was found in less than 9 h. Their findings show that the MFC with Fenton system can be used to remediate paracetamol-containing wastewater in an energy-efficient and effective manner.

Neomycin sulfate, one of the antibiotics, was quantified in MFCs in an indirect manner. The elimination of neomycin sulfate tracked using LC-MS/MS with total carbohydrate clearance and COD. While the partial degradation of neomycin sulfate was observed, it appeared to have an impact on the performance of MFCs and eventually limited the MFC performance in a concentration-dependent mode. MFCs based on electroactive biofilm may be used with high specificity to assess the neomycin sulfate in wastewater [54].

A single-chambered MFC fed with different combinations of penicillin and glucose-based synthetic wastewater [55] investigated the effect of penicillin on the generation of power. In just 24 h, 98% of penicillin had degraded. These MFC

performance data suggested that penicillin may have aided the transfer of electrons to the anode from the bacterial cell by boosting the cell membrane's electron permeability. Similar tests on a glucose–ceftriaxone sodium mixture showed that ceftriaxone sodium breakdown efficiency was 91% in 24 h, compared to 51% in the control anaerobic reactor. With different antibiotics and their substrates, synergistic and antagonistic effects such as inhibition of power generation have been identified. These studies show that microorganisms' mechanisms of action differ with ecosystems, antibiotics, and the substrates used [56]. Antibiotic elimination rose by 10–35% with a charge output of 940–1132 C, according to [57]. To adapt to enhanced antibiotic clearance, functional microorganisms changed in closed and open-circuit treatments and microbial affinities increased by 340% and 50%, respectively. Wang et al. [50] investigated the SDZ elimination in MFCs in terms of operation of MFC, reaction mechanism, degradation products, removal of SDZ biotoxicity, and the relationship between SDZ removal with microbial community in a paper published in 2018. SDZ would have a significant impact on reactor microbe activity and SDZ biodegradation in MFCs requires long-term acclimatization. After acclimation, a rate of 10 mg/L of SDZ could be eliminated within 48 h. After examining the microbial community in the reactor, the dominance of Mycobacterium, Methanocorpusculum, Clostridium, Enterobacter, Thiobacillus, Stenotrophomonas, and Pseudomonas was highly associated with the elimination of SDZ at different operation cycles throughout the experiment. According to [58], the most dominant genus near the bioanode was aromatic degrading Thauera (56.4%).

14 MFC for a Sustainability Future

The use of microorganisms for the remediation of toxic pharmaceutical pollutants plays a major role. The diversity in substrate used, organisms and physiochemical treatment conditions result in green electricity production. To meet the sustainable development goals, this technology has its own benefits. However, major studies on a large-scale basis are lacking. A detailed review of the substrates, conditions, and the yield of electricity is given by Deepak [59]. Further research is warranted in this area to upscale the process and to make it commercially feasible. The use of microbial enzymes and immobilized enzymes in MFC also needs to be studied. Using MFC in an efficient way will convert recalcitrant pollutants into biodegradable, nontoxic chemicals. The use of microbial consortia in MFC can give better results than individual organisms. The compatibility of organisms and their synergistic effects also requires analysis in wastewater treatment process.

15 Conclusion

MCF has tremendous opportunities in future in the removal of even recalcitrant pharmaceutical pollutants because it degrades organic and inorganic wastes and at the same time results in the generation of power for the plant operation. It can be integrated with the waste treatment plants of pharmaceutical industries for in situ bioremediation; thereby entry of pharmaceutical pollutants into the environment can be curtailed. Little research on scaling up the process has shown promising results. Further innovation in building the MCF technology and its economic viability would help achieve real-time applications, thus yielding a sustainable waste treatment process.

References

1. Randhawa GK, Kullar JS (2011) Bioremediation of pharmaceuticals, pesticides, and petrochemicals with gomeya/cow dung. ISRN Pharmacol, 362459. https://doi.org/10.5402/2011/362459
2. Durrant C (2001) The responsibility of the pharmaceutical industry. Clin Microbiol Infect 7(6):2–4
3. Cecconet D, Molognoni D, Callegari A, Capodaglio AG (2017) Biological combination processes for efficient removal of pharmaceutically active compounds from wastewater: a review and future perspectives. J Environ Chem Eng 5(4):3590–3603
4. Chelliapan S, Wilby T, Yuzir A, Sallis P (2011) Influence of organic loading on the performance and microbial community structure of an anaerobic stage reactor treating pharmaceutical wastewater. Desalination 271:257–264. https://doi.org/10.1016/j.desal.2010.12.045
5. Ramola B, Singh A (2013) Heavy metal concentrations in pharmaceutical effluents of industrial area of Dehradun (Uttarakhand), India. J Environ Anal Toxicol 03. https://doi.org/10.4172/2161-0525.1000173
6. Vuppala NS, Suneetha C, Saritha V (2012) Study on treatment process of effluent in bulk drug industry. Int J Res Pharm Biomed Sci 3(3), 1102–1095
7. Kar D, Sur P, Mandal SK, Saha T, Kole RK (2008) Assessment of heavy metal pollution in surface water. Int J Environ Sci Technol 5(1):119–124
8. Wise R (2002) Antimicrobial resistance: priorities of action. J Antimicrob Chemother 49(4):585–586
9. Rana RS, Singh P, Kandari V et al (2017) A review on characterization and bioremediation of pharmaceutical industries' wastewater: an Indian perspective. Appl Water Sci 7:1–12. https://doi.org/10.1007/s13201-014-0225-3
10. Rajasulochana P, Preethy V (2016) Comparison on efficiency of various techniques in treatment of waste and sewage water—A comprehensive review. Resour-Effic Technol 12(4):175–184
11. Caliman FA, Gavrilescu M (2009) Pharmaceuticals, personal care products and endocrine disrupting agents in the environment—A review. Clean 37(4–5):277–303. https://doi.org/10.1002/clen.200900038
12. Spring AJ, Bagley DM, Andrews RC, Lemanik S, Yang P (2007) Removal of endocrine disrupting compounds using a membrane bioreactor and disinfection. J Environ Eng Sci 6(2):131–137. https://doi.org/10.1139/s06-049
13. Arboleda C, Cabana H, De Pril E, Jones JP, Jiménez GA, Mejía AI, Agathos SN, Penninckx MJ (2013) Elimination of bisphenol A and triclosan using the enzymatic system of autochthonous Colombian forest fungi. Biotechnology 1–12. https://doi.org/10.5402/2013/968241

14. Wesenberg D, Kyriakides I, Agathos SN (2003) White-rot fungi and their enzymes for the treatment of industrial dye effluents. Biotechnol Adv 22(1–2):161–187
15. Bagchi S, Behera M (2020) Evaluating the effect of the antibiotic ampicillin on performance of a low-cost microbial fuel cell. J Hazard Toxic Radioact Waste 24(3)
16. Potter MC (1911) Electrical effects accompanying the decomposition of organic compounds. Proc R Soc Lond B Biol Sci 84:260–276
17. Idris SA, Esat FN, Rahim AAA, Rizzqi WAZ, Ruzlee W, Razali WMZ (2016) Electricity generation from the mud by using microbial fuel cell. In: MATEC web of conferences 69:02001. https://doi.org/10.1051/matecconf/20166902001
18. Khan N, Anwer AH, Ahmad A, Sabir S, Khan MZ (2020) Investigating microbial fuel cell aided bio-remediation of mixed phenolic contaminants under oxic and anoxic environments. Biochem Eng J 155. https://doi.org/10.1016/j.bej.2019.107485
19. Zhou Z, Liu X, Sun K, Lin C, Ma J, He M, Ouyang W (2019) Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: a review. Chem Eng J 372:836–851
20. Obileke KC, Onyeaka H, Meyer EL, Nwokolo N (2021) Microbial fuel cells, a renewable energy technology for bio-electricity generation: a mini-review. Electrochem Commun 125. https://doi.org/10.1016/j.elecom.2021.107003
21. Araneda I, Tapia NF, Lizama Allende K, Vargas IT (2018) Constructed wetland-microbial fuel cells for sustainable greywater treatment. Water 10(7):940
22. Asim AY, Mohamad N, Khalid U, Tabassum P, Akil A, Lokhat D, Siti H (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214:379–389
23. Yaqoob AA, Mohamad Ibrahim MN, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) Recent advances in anodes for microbial fuel cells: an overview. Materials 13(9):2078
24. Yaqoob AA, Khatoon A, Mohd Setapar SH, Umar K, Parveen T, Ibrahim MNM, Rafatullah M (2020b) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10(8):819
25. Wang L, Liu Y, Wang C, Zhao X, Mahadeva GD, Wu Y, Ma J, Zhao F (2017) Anoxic biodegradation of triclosan and the removal of its antimicrobial effect in microbial fuel cells. J Hazard Mater 344. https://doi.org/10.1016/j.jhazmat.2017.10.021
26. Umar MF, Rafatullah M, Abbas SZ, Ibrahim MN, Ismail N (2021) Bioelectricity production and xylene biodegradation through double chamber benthic microbial fuel cells fed with sugarcane waste as a substrate. J Hazard Mater 419. https://doi.org/10.1016/j.jhazmat.2021.126469
27. Adelaja O, Keshavarz T, Kyazze G (2014) Enhanced biodegradation of phenanthrene using different inoculum types in a microbial fuel cell. Eng Life Sci 14(2)
28. Fu C-C, Su C-H, Hung T-C, Hsieh C-H, Suryani D, Wu W-T (2009) Effects of biomass weight and light intensity on the performance of photosynthetic microbial fuel cells with Spirulina platensis. Biores Technol 100(18):4183–4186
29. Baicha Z, Salar-García MJ, Ortiz-Martínez VM, Hernández-Fernández FJ, De los Ríos AP, Labjar N, Lotfi E, Elmahi M (2016) A critical review on microalgae as an alternative source for bioenergy production: a promising low cost substrate for microbial fuel cells. Fuel Process Technol 154:104–116
30. Khandelwal A, Chhabra M, Yadav P (2020. Performance evaluation of algae assisted microbial fuel cell under outdoor conditions. Bioresour Technol 310:123418
31. Gajda I, Greenman J, Melhuish C, Ieropoulos I (2015) Self-sustainable electricity production from algae grown in a microbial fuel cell system. Biomass Bioenergy 82:87–93
32. Powell EE, Mapiour ML, Evitts RW, Hill GA (2009) Growth kinetics of Chlorella vulgaris and its use as a cathodic half cell. Bioresour Technol 100(1):269–274
33. Lan J-W, Raman K, Huang C-M, Chang C-M (2013) The impact of monochromatic blue and red LED light upon performance of photo microbial fuel cells (PMFCs) using Chlamydomonas reinhardtii transformation F5 as biocatalyst. Biochem Eng J 78:39–43. https://doi.org/10.1016/j.bej.2013.02.007

34. Xu C, Poon K, Choi MM, Wang R (2015) Using live algae at the anode of a microbial fuel cell to generate electricity. Environ Sci Pollut Res Int 22(20):15621–15635
35. Vinayak V, Khan MJ, Varjani S, Saratale GD, Saratale RG, Bhatia SK (2021) Microbial fuel cells for remediation of environmental pollutants and value addition: special focus on coupling diatom microbial fuel cells with photocatalytic and photoelectric fuel cells. J Biotechnol 338:5–19
36. Sambavi S, Vishali S, Varjani S, Mullai P (2020) Electricity generation in a microbial fuel cell using iron oxide nanoparticles. Indian J Exp Biol (IJEB) 58(08):571–577
37. Mohamed SN, Hiraman PA, Muthukumar K, Jayabalan T (2020) Bioelectricity production from kitchen wastewater using microbial fuel cell with photosynthetic algal cathode. Bioresour Technol 295. https://doi.org/10.1016/j.biortech.2019
38. Liu T, Rao L, Yuan Y, Zhuang L (2015) Bioelectricity generation in a microbial fuel cell with a self-sustainable photocathode. Sci World J
39. Nishio K, Hashimoto K, Watanabe K (2013) Digestion of algal biomass for electricity generation in microbial fuel cells. Biosci Biotechnol Biochem, 120833
40. Fu X, Fu L, Marrani HI (2020) A Novel adaptive sliding mode control of microbial fuel cell in the presence of uncertainty. J Electr Eng Technol, 1–8. https://doi.org/10.1007/s42835-020-00535-1
41. Lakaniemi A-M, Hulatt CJ, Thomas DN, Tuovinen OH, Puhakka JA (2012) Biogenic hydrogen and methane production from Chlorella vulgaris and Dunaliella tertiolecta biomass. Biotechnol Biofuels 4:34
42. Lakshmidevi R, Gandhi NN, Muthukumar K (2020) Carbon neutral electricity production from municipal solid waste landfill leachate using algal-assisted microbial fuel cell. Appl Biochem Biotechnol, 1–15
43. Elakkiya E, Niju S (2020) Simultaneous treatment of lipid rich ghee industry wastewater and power production in algal biocathode based microbial fuel cell. Energy Sourc Part A Recov Util Environ Eff, 1–11
44. Abazarian E, Gheshlaghi R, Mahdavi MA (2020) Impact of light/dark cycle on electrical and electrochemical characteristics of algal cathode sediment microbial fuel cells. J Power Sour 475:228686
45. Zhang Y, Liu M, Zhou M, Yang H, Liang L, Gu T (2019) Microbial fuel cell hybrid systems for wastewater treatment and bioenergy production: synergistic effects, mechanisms and challenges. Renew Sustain Energy Rev 103:13–29
46. Zhang Y, Zhao Y, Zhou M (2019) A photosynthetic algal microbial fuel cell for treating swine wastewater. Environ Sci Pollut Res Int 26(6):6182–6190
47. Gadhamshetty V, Belanger D, Gardiner C-J, Cummings A, Hynes A (2013) Evaluation of Laminaria-based microbial fuel cells (LbMs) for electricity production. Bioresour Technol 127:378–385
48. Vinayak V, Joshi KB, Sarma PM (2019) Diafuel^{TM}(diatom biofuel) versus electric vehicles, a basic comparison: a high potential renewable energy source to make india energy independent. Diatoms: Fundam Appl, 537–582
49. Ali J, Wang L, Waseem H, Song B, Djellabi R, Pan G (2020) Turning harmful algal biomass to electricity by microbial fuel cell: a sustainable approach for waste management. Environ Pollut 266:115373
50. Wang L, Liu Y, Wang C, Zhao X, Mahadeva GD, Wu Y, Ma J, Zhao F (2018) Anoxic biodegradation of triclosan and the removal of its antimicrobial effect in microbial fuel cells. J Hazard Mater 344:669–678. https://doi.org/10.1016/j.jhazmat.2017.10.021
51. Zhang Q, Zhang Y, Li D (2017) Cometabolic degradation of chloramphenicol via a meta-cleavage pathway in a microbial fuel cell and its microbial community. Bioresour Technol 229:104–110. https://doi.org/10.1016/j.biortech.2017.01.026
52. Wang L, Liu Y, Ma J, Zhao F (2016) Rapid degradation of sulphamethoxazole and the further transformation of 3-amino-5-methylisoxazole in a microbial fuel cell. Water Res 88:322–328. https://doi.org/10.1016/j.watres.2015.10.030

53. Zhang B, Wang Z, Zhou X, Shi C, Guo H, Feng C (2015) Electrochemical decolorization of methyl orange powered by bioelectricity from single-chamber microbial fuel cells. Biores Technol 181:360–362. https://doi.org/10.1016/j.biortech.2015.01.076
54. Catal T, Yavaser S, Enisoglu-Atalay V, Bermek H, Ozilhan S (2018) Monitoring of neomycin sulfate antibiotic in microbial fuel cells. Biores Technol 268:116–120
55. Wen Q, Yang L, Zhao Y, Huang L, Chen Z (2018) Insight into effects of antibiotics on reactor performance and evolutions of antibiotic resistance genes and microbial community in a membrane reactor. Chemosphere 197:420–429. https://doi.org/10.1016/j.chemosphere.2018.01.067
56. Zhou Y, Zhu N, Guo W, Wang Y, Huang X, Pingxiao W, Dang Z, Zhang X, Xian J (2018) Simultaneous electricity production and antibiotics removal by microbial fuel cells. J Environ Manag 217:565–572
57. Zhao X, Li X, Li Y et al (2019) Shifting interactions among bacteria, fungi and archaea enhance removal of antibiotics and antibiotic resistance genes in the soil bioelectrochemical remediation. Biotechnol Biofuels 12:160. https://doi.org/10.1186/s13068-019-1500-1
58. Miran W, Jang J, Nawaz M, Shahzad A, Lee DS (2018) Biodegradation of the sulfonamide antibiotic sulfamethoxazole by sulfamethoxazole acclimatized cultures in microbial fuel cells. Sci Total Environ 627:1058–1065
59. Pant D, Van Bogaert G, Diels L, Vanbroekhoven K (2009)A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresour Technol 101(6):1533–1543. https://doi.org/10.1016/j.biortech.2009.10.017
60. Chang C-Y, Chang J-S, Vigneswaran S, Kandasamy J (2008) Pharmaceutical wastewater treatment by membrane bioreactor process—A case study in Southern Taiwan. Desalination 234(1–3):393–401. https://doi.org/10.1016/j.desal.2007.09.109
61. Fu C-C, Hung T-C, Wu W-T, Wen T-C, Su C-H (2010) Current and voltage responses in instant photosynthetic microbial cells with Spirulina platensis. Biochem Eng J 52(2–3):175–180
62. Kadam A, Patil S, Patil S, Tumkur A (2016) Pharmaceutical waste management an overview. Indian J Pharm Pract 9(1):3
63. Kondaveeti S, Choi KS, Kakarla R, Min B (2014) Microalgae Scenedesmus obliquus as renewable biomass feedstock for electricity generation in microbial fuel cells (MFCs). Front Environ Sci Eng 8(5):784–791
64. Rodgers-Vieira EA, Zhang Z, Adrion AC, Gold A, Aitken MD (2015) Identification of anthraquinone-degrading bacteria in soil contaminated with polycyclic aromatic hydrocarbons. Appl Environ Microbiol 81(11):3775–3781. https://doi.org/10.1128/AEM.00033-15
65. Mandal SK, Das N (2018) Application of microbial fuel cells for bioremediation of environmental pollutants: an overview. J Microbiol Biotech Food Sci/Mandal Das 7(4):437–444
66. Smułek W, Zdarta A, Guzik U, Dudzińska-Bajorek B, Kaczorek E (2015) Rahnella sp. strain EK12: cell surface properties and diesel oil biodegradation after long-term contact with natural surfactants and diesel oil. Microbiol Res 176:38–47. https://doi.org/10.1016/j.micres.2015.04.008

Bioremediation of Petrochemicals and Dye Industrial Effluents through Microbial Fuel Cells

R. Merlyn Sujatha, L. Monisha Mary, and J. Jayapriya

1 Introduction

A fuel cell that uses microorganisms as catalysts for the oxidation of substrates, leading to electricity generation, is termed a microbial fuel cell (MFC). They are deployed for sustainable energy production, treatment of wastes, and minimizing CO_2 emissions. There is a compelling need for energy- and cost-efficient alternates to the conventional wastewater treatment systems due to their high energy requirements. Domestic and industrial effluents contain a multitude of organic compounds that can fuel MFCs, and the microbes in MFCs can accomplish both pollutant degradation and power generation in parallel. Moreover, it minimizes solid disposal by 50–90% [23] and hence is generally accepted as a promising sustainable biotechnological solution to future energy requirements. However, it is yet to be commercially exploited since there are many hurdles to be overcome. This chapter mainly focuses on the application of MFCs toward the removal of environmental pollutants, such as synthetic dyes and polycyclic aromatic compounds. Recent progress in the understanding of system architecture, anode/cathode materials, and biocatalysts employed in MFCs for pollutant degradation to achieve high energy density has been reviewed.

R. M. Sujatha · L. M. Mary · J. Jayapriya (✉)
Department of Applied Science and Technology, AC Tech, Anna University, Chennai 600025, India
e-mail: jayapriyachem@gmail.com

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_12

2 Bioremediation of Petrochemicals Through Microbial Fuel Cells

The ever-growing global economy and population have ensured an increasing demand for petroleum products, thus aiding the growth and multiplication of relevant industries worldwide [101]. The environmental impact of petroleum products is a correspondingly vast and extensive field. Petroleum hydrocarbons are harmful to many soil organisms and humans. This fossilized fuel has become a necessary source of energy since the late nineteenth century due to elevated consumption globally. The petrochemical industry involves the production of solvents, resins, lubricants, and plastics, generating wastewater containing toxic compounds [79]. In the downstream sector, wastewater from petroleum industries and refineries contains phenolic compounds, aromatic hydrocarbons, salts, alkanes, naphthalene, nitrobenzene, oil, and grease. These pollutants are toxic, not biodegradable, and carcinogenic [17]. In the upstream sector, the exploration and production process of conventional crude oil generates the largest volume of waste stream termed Produced water (PW). Typically, PW contains emulsified oils besides a high amount of sodium chloride, carbonates of magnesium, sulfates, and other inorganic dissolved and suspended solids. Benzene, xylenes, ethylbenzene, and toluene are hazardous chemicals, also known as BTEX materials. They are a threat to human health and are common PW water contaminants [121]. Petroleum product contamination degrades the ecological structure and function of the soil, affecting moisture, pH, carbon/nitrogen ratio, and porosity. As the pollutant concentration rises, the hydrophobicity increases, thereby inhibiting the seed germination [39]. The aromatic hydrocarbon groups of compound derivatives have molecular rings, including benzene rings. Usually, instead of a hydrogen atom in the benzene ring, methyl or ethyl groups are found (toluene, methyl/dimethyl benzene and ethylbenzene) [92]. These hydrocarbons, referred to as polycyclic aromatic hydrocarbons (PAHs), can cause musculoskeletal malformation and bone marrow suppression [93]. PAHs toxicology and physicochemical characteristics are varied according to their molecular weight [104]. Recent studies demonstrate that benzenes can easily bind to soil particles, and BTEX chemical compounds need sufficient oxygen to break down slowly. These compounds are volatile and hence can affect the human respiratory system [58]. Hence, researchers have taken great efforts to upgrade the different technologies used to treat wastewater from the petroleum industry, such as adsorption, coagulation, membrane separation process, dissolved air flotation, and chemical destabilization [103]. However, these unit operations are ineffective for the treatment of petroleum wastewater because of the complexity of PAHs. Although incineration and chemical oxidation can remove up to 99.0 and 92.3% of the total petroleum hydrocarbons from wastewater, respectively, both these restoration procedures have disadvantages. Toxic substances, such as dioxins, furans, polychlorinated biphenyls, and volatile heavy metals, are released into the atmosphere as a result of the incomplete burning of crude oils [19]. Therefore, an effective remediation measures should be tailored considering the human health and ecosystem management.

The biological treatment of petroleum wastewater can be accomplished by aerobic and anaerobic processes. However, the anaerobic process is preferred over aerobic due to lower energy consumption and less sludge production, though it is time-consuming [1, 102]. Bioelectrochemical systems (BES) are versatile [89] because, in contrast to typical bioreactors, they can concurrently generate electricity and treat wastewater. Similarly, in recent years, an emerging technology based on biostimulation, namely microbial fuel cells (MFCs), has been demonstrated to remove PAHs from soils and sediments.

2.1 MFCs for Petroleum Product Degradation

2.1.1 In-Situ Bioremediation of PAH-Contaminated Soil in Microbial Fuel Cells

In situ bioremediation is a biological treatment method to clean up PAHs present in the environment. The potential advantages of in-situ bioremediation are (i) minimal site disruption, (ii) continuous treatment of contaminated soil and groundwater, and (iii) economical. The anaerobic degradation of petroleum compounds has been identified in a wide spectrum of microbial pathways, including denitrification [4, 51], metal reduction [52], and sulfate reduction [84]. MFC configurations with different electrode materials for in-situ bioremediation to remove hydrocarbons from soils and sediments as shown in Table 1. Yuan et al. [113] developed a tubular air-cathode MFC (TAC-MFC) with a cloth cathode assembly and utilized organic sediment as the substrate, demonstrating the highest power density of 107.1 ± 8.6 mW/m^2, coulombic efficiency of 17.9%, and the lowest internal resistance (20 Ω). Bioremediation of PAHs in sediments through MFC technology is shown in Fig. 1; the anodic reactions include the oxidation of organic matter, sulfides, and other potential pollutants. The color of the sediment apparently turned from black to brown after MFC operation in the contaminated sites. Huang et al. [25] reported enhanced phenol biodegradation and simultaneous electricity production from organic pollutants in a soil MFC (Fig. 2). An in-situ MFC was inserted into waterlogged anoxic soil for the remediation of organic pollutants, and the power reached 29.45 mW/m^2 with 90.1% removal of phenol. The phenol degradation rate in this BES was approximately 23 times higher than biological treatment. Similarly, another bioelectrochemical treatment (BET) system showed 41.08% petroleum hydrocarbon removal compared to 20.72% obtained using conventional anaerobic treatment with petroleum sludge as the substrate [59]. Wang et al. [105] demonstrated a U-tube MFC for the bioremediation of PAHs-contaminated soil. Due to the presence of exoelectrogenic biofilms on the surface of the anode, it could effectively remove *n*-alkanes and PAHs from the soil. However, the power density was low ($0.85 + 0.05$ mW/m^2), suggesting that the U-tube air-cathode MFC was not as suitable for soil remediation systems.

To increase the degradation efficiency of total petroleum hydrocarbons (TPH) [117], varied the arrangement of anodes from vertical to a horizontal position in a

Table 1 MFC for treatment of petroleum refinery water effluent

S.No	Petroleum products	Co-substrate	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
1.	Groundwater hydrocarbons	Glucose	Stainless steel	Carbon cloth	Single-cell MFC	120 (mW/m^2)	–	Morris and Jin [66]
2.	Quinoline	Glucose	Carbon	Air	Dual-chambered MFC	16.4 (mW/m^2)	Removal: 200 mg/L	Zhang et al. [114, 116]
3.	Hydrocarbon-contaminated groundwater	–	Carbon	Pt catalyst	Dual-chambered MFC	1.25 (mW/m^2)	COD: 65.6%	Adelaja et al. [2]
4.	Petroleum Hydrocarbon-contaminated waste water	–	Carbon cloth	Platinised-carbon cloth	Dual-chambered MFC	1.06 (mW/m^2)	COD Removal: 79.1%; degradation rate: 91.6%	Adelaja et al. [3]
5.	Complex petrochemical wastewater	–	Stainless steel mesh	Graphite plate	Single chambered BET system	Anoxic: 17.1 (mW/m^2) and Aerobic: 14.3 (mW/m^2)	Substrate degradation: 3.34 kg COD/m^3-day	Yeruva et al. [112]
6.	Ethylene glycol	Glucose	Graphite sheet	Pt sheet	Single chamber MFC	5.72 (mW/m^2)	COD: 92–98%	Hosseinpour et al. [24]
7.	Petrochemical wastewater	–	Carbon cloth	Pt coated carbon cloth	Single chamber MFC	225 ± 1.4 (mW/m^2)	COD: 84.4% and 95% oil removal	Srikanth et al. [94]
8.	Petrochemical wastewater	Acetate	Graphite cylinder	Graphite cylinder	Single chamber graphite BES	222 (mW/m^2)	TPH: 90% COD: 34.9%	Mohanakrishna et al. [60–62]

(continued)

Table 1 (continued)

S.No	Petroleum products	Co-substrate	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
9.	Petroleum refinery wastewater	–	Graphite fiber	Pt coated carbon cloth	Single chamber air-cathode MFC	45 (mW/m^2)	Removal of TPH: 89% COD: 41.2%	Mohanakrishna et al. [60–62]
10.	Petroleum refinery wastewater	Acetate	Bioanode	Biocathode	Single chamber hybrid based BES	Batch mode: 725 (mW/m^2) *continuous mode*: 561 (mW/m^2)	Batch mode: COD: 69.2% *continuous mode*: COD: 37%	Mohanakrishna et al. [60–62]
11.	2,4-dichlorophenol	Glucose	Carbon cloth	Platinised titanium (Pt/Ti) catalyst plate	Dual chamber MFC	37 (mW/m^2)	COD: 41%	Hassan et al. [22]
12.	Petrochemical wastewater	–	Polyacrylonitrile coated carbon felt	Polyacrylonitrile coated carbon felt	Dual chamber MFC	850 (mW/m^2)	COD: 40%	Sarmin et al. [87]
13.	Petroleum produced water	–	Graphite brush	Platinum coated carbon cloth	Dual chamber MFC	1089 (mW/m^2)	sulfate: 93.9%, TPH: 53.1%, COD: 60.2%	Mohanakrishna et al. [64, 65]
14.	Petroleum refinery wastewater	–	Carbon fiber brush	Carbon cloth	Osmotic microbial fuel cell and up-flow microbial desalination cell	84 (mW/m^2)	COD: 93%	Sevda and Abu-Reesh [88]

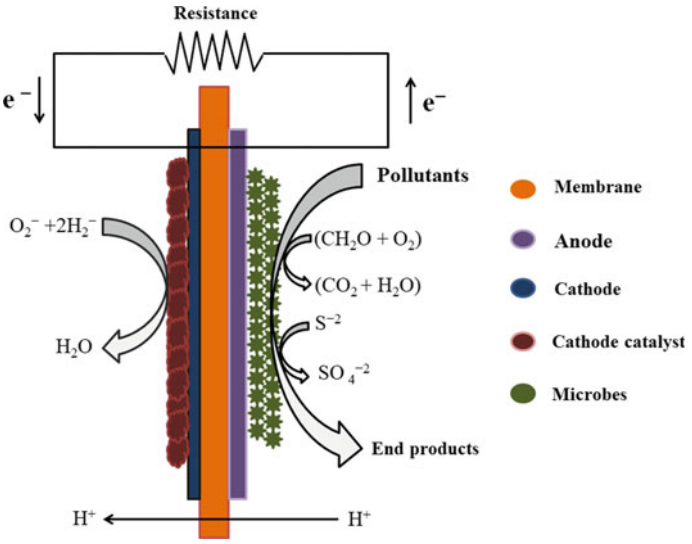

Fig. 1 Illustrative bioremediation mechanics of sediments in MFC. Adapted from Yuan et al. [113]

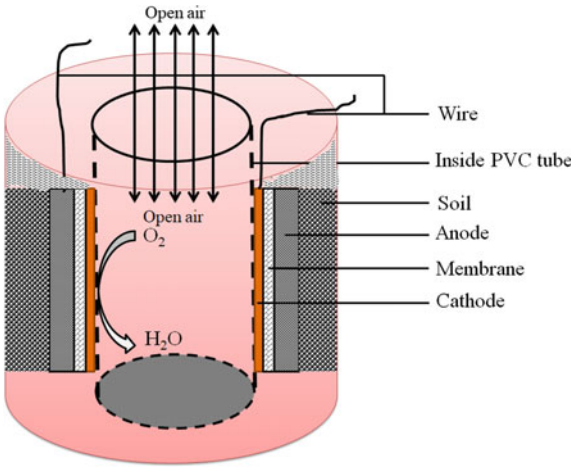

Fig. 2 Schematic representation of Tubular air-cathode MFC (TAC–MFC) Adapted from Huang et al. [25]

soil MFC (Fig. 3 and found that the horizontally arranged anodes (50.6% showed superior performance than the vertical counterparts (8.3%. Charge output was also higher in the horizontal anode configuration (833 C compared with the vertical mode (762 C. The PAH degradation rate increased from 2 to 24% in 66 d; however, low power output was observed in the in-situ MFCs with vertical anodes (an average of 37 mWm^{-3}). In most cases, the internal resistance of the in-situ MFC was high was

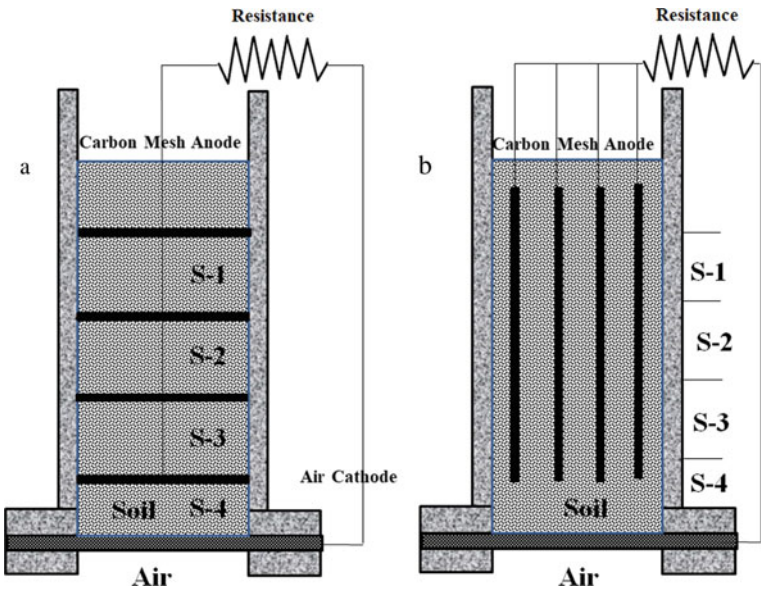

Fig. 3 Figurative representation of soil MFC (A) vertically arranged anodes and (B) horizontally arranged anodes. Adapted from Zhang et al. [117]

mainly due to the high ohmic resistance i.e., low soil conductivity and mass transfer limitations [67]. To overcome these issues, the amendment of PAH-contaminated soil with different additives, such as sand, carbon fibers, and biochar, was adapted to enhance the bioelectrochemical remediation of PAHs. Amendment with sand increased the soil porosity from 44.5 to 51.3%, decreased Ohmic resistance by 46%, and increased the charge output from 2.5 to 3.5 C g^{-1} [42]. The porosity of the soil plays a significant role in increasing both dissolved oxygen content and proton transport, thereby decreasing charge transfer resistance. Moreover, the internal resistance of the soil MFC decreased by 58% after mixing 1% carbon fiber with the soil samples, leading to a 15-fold increment in electricity production and 329% higher removal of petroleum hydrocarbons [44, 45]. Similarly, the addition of biochar with high N content accelerated the selective enhancement of the bacterial community and exhibited the best efficiency in the removal of recalcitrant contaminants, such as aromatics [47]. A plant microbial fuel cell (PMFC) is a promising modified MFC that fosters plant-microbe relationship at the rhizosphere region of a plant, which consequently increases the biofilm adhesion on the anode, thereby improving electron transfer from the biofilm to the anodes in the PMFC. The synergistic action of plants and surfactants significantly enhances the efficiency of the MFC system in the removal of petroleum from the soil and encourages the applications of P-MFCs for the in-situ remediation of petroleum-contaminated soils. Zhao et al. [118] used plant MFC to degrade phenanthrene and pyrene in contaminated soils. The addition of surfactant β-cyclodextrin enabled the desorption of PAHs from the soil to the plant

at a higher rate than Tween 80 and decreased the charge transfer resistance by 63.4%. This suggests that the amendment of contaminated soil with some additives, which possess the characteristics of conductivity and micronutrient, enhances the removal of petroleum from the soil in MFC systems.

2.1.2 Bioremediation of Petroleum Wastewater in MFCs

Petroleum hydrocarbons are very common groundwater contaminants that usually deplete oxygen when they undergo biodegradation. The anaerobic degradation of petroleum compounds has been identified to involve a wide spectrum of microbial pathways, including denitrification [4, 51], metal reduction [52], and sulfate reduction [84]. The bioremediation of petroleum waste, including wastewater from petroleum refineries, petroleum sludge, and oil-contaminated soil, has been studied in MFCs (Table 2). The downstream petroleum refinement processes generate large volumes of wastewater containing hydrocarbons, such as phenols, benzene, and xylenes, as well as inorganic compounds, such as ammonia, nitrite, sulfides, and heavy metals. Wastewater from petroleum refineries can range from 0.4 to 1.6 times the volume produced during crude oil processing [9] The low BOD/COD ratio (<0.2) and high total dissolved solids (TDS) render the petroleum refinery wastewater (PRW) unsuitable for biological treatment.

In 2008, Morris and Jin reported, for the first time, MFC technology for the degradation of hydrocarbon contaminants in groundwater under anaerobic conditions. Using refinery wastewater as the sole substrate, they achieved power generation (as high as 120 mW/m^2 at the cathode) in approximately ~6 d with a single cell MFC. It is known that the larger the electrode spacing, the potential losses in the cell are higher. The authors reported that the cell potential decreased by ~55% over a 9 m-long proton bridge, with a 6.9% decrease in potential per meter of the bridge [66]. To enhance the treatment of PRW in a single-chamber air-cathode microbial fuel cell (MFC), external voltage from 100 to 500 mV was applied to the electrochemically active anodic biofilm [60–62]. The MFC operated with 500 mV supplemental voltage exhibited a maximum power density of 132 mW/m^2, which was three times higher than control MFC (45 mW/m^2). Similarly, the highest substrate removal efficiency (48%) was obtained with the MFC supplemented by 500 mV, followed by those supplied with 300 mV (37%), 100 mV (32%), and the 0 V control (27%). Therefore, the applied potential enhanced the diesel-range organics (DROs)/straight chain-alkane degradation efficiency. [88] proposed the coupling of a hydraulically connected osmotic microbial fuel cell (OsMFC) and an up-flow microbial desalination cell (UMDC) for enhanced PAH removal, along with high power output in the MFC and simultaneous seawater desalination in the UMDC (Fig. 4). Both OsMFC and UMDC were connected to 100 Ω external resistance, and the system achieved 93% chemical oxygen demand (COD) removal from the petroleum refinery wastewater besides 48% salt removal from the seawater. Sarmin et al. [87] treated the petroleum chemical wastewater from an acrylic acid plant using an MFC, which generated 850 mW/m^2 maximum power density at 1500 mA/m^2 current density and

Table 2 In situ MFC for bioremediation of PAHs-contaminated soil

S.No	Petroleum products	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
1.	Organic rich sediment	Carbon felt	Canvas cloth	Tubular air-cathode MFC (TAC-MFC)	107.1 ± 8.6 (mW/m^2)	LOI: 33.1% ROOM: 36% AVS: 94.9%	Yuan et al. [113]
2.	Organic pollutants	Carbon felt	Conductive paint + catalyst	Soil MFC	29.45 (mW/m^2)	SCOD (mg/L): 430 TCOD (mg/L): 35,500	Huang et al. [26]
3.	Petrochemical sludge	Graphite plates	Open-air	Single chamber MFC	53.11 (mW/m^2)	41.08% of TPH	Mohan and Chandrasekhar [59]
4.	Petroleum sludge	Non-catalyzed graphite plates	Air	Single chambered BET system	20.62 (mW/m^2); 198.31 (mA/m^2)	58 (aromatics at 30 g TPH/L) 70 (aromatics at 3 g TPH/L)	Chandrasekhar and Venkata Mohan [7]
5.	Petroleum contaminated sediments	Carbon cloth	Carbon paper/platinum (Pt)	Sediment MFC	2162 (mW/m^3)	16,000 mg/kg sediment	Morris and Jin [67]
6.	Phenanthrene and pyrene in freshwater sediments	Stainless steel	Stainless steel	Sediment MFC	–	*Removal*: Phenanthrene: 99.47 ± 0.15% Pyrene: 94.79 ± 0.63%	Yan et al. [109]
7.	Petroleum Hydrocarbon contaminated saline soil	Carbon mesh	Air	U-Tube MFC	0.85 ± 0.05 (mW/m^2)	TPH: 0.3–2.5%	Wang et al. [105]

(continued)

Table 2 (continued)

S.No	Petroleum products	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
8.	Petroleum hydrocarbon soil	Carbon mesh	Air	Soil MFC	37 (mW/m^2)	TPH: 120%	Li et al. [41]
9.	Hydrocarbon-contaminated soil	Carbon cloth	Air	Soil Tubular BES	39.1 (mW/m^2)	TPH removal: 78.7%	Lu et al. [53]
10.	Polycyclic aromatic hydrocarbons (PAHs)	Plain graphite plate	Graphite felt	Sediment MFC	0.4–0.6 V	22.1% (TOC removal in closed circuit)	Yang et al. [111]
11.	Benzo(*a*)pyrene, pyrene in sediments	Graphite felt	Graphite felt	Sediment MFC	64.8 mV	Degradation rate: 70%	Yan et al. [110]
12.	Petroleum hydrocarbon-contaminated soil	Carbon mesh	Air	Air-cathode soil MFC	–	TPH degradation: 15.3 ± 0.2%	Zhang et al. [117]
13.	Polycyclic aromatic hydrocarbons (PAHs) in sediments	Graphite plate	Graphite plate	Sediment MFC	Anaerobic: 2 (mW/m^2) and Aerobic: 5.8 (mW/m^2)	(Anaerobic environment) removal: 76.9% of Naphthalene, 52.5% of acenaphtene and 36.8% of phenanthrene TOC: 67%	Sherafatmand and Ng [91]
14.	Petroleum hydrocarbon-contaminated soil	Carbon mesh	Air	Soil MFC	–	Degradation of petroleum hydrocarbons(PH) upto 268%	Li et al. [42]

(continued)

Table 2 (continued)

S.No	Petroleum products	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
15.	Petroleum Hydrocarbons in soil	Carbon mesh	Activated carbon air-cathode	Soil MFC	43 (mW/m^2)	–	Li et al. [44, 45]
16.	Petroleum hydrocarbon-contaminated soil	Carbon mesh	Air	Soil MFC	304 (mA/m^2)	Degradation rate: 484%	Li et al. [44, 45]
17.	Petroleum hydrocarbon-contaminated soil	Graphite rod	Carbon air-cathode	Soil MFC	0.8 (mW/m^2)	TPH: 100%	Li et al. [44, 45]
18.	Petroleum hydrocarbon-contaminated soil	Carbon cloth	Carbon cloth	Dual chamber MFC	220 (mW/m^2)	–	Zhou et al. [120]
19.	Petroleum hydrocarbon-contaminated aged soil	Carbon mesh	Air	Soil MFC	153.8 ± 0.1 mA m^{-2}	bioelectricity generation rate: 0.321 C d^{-1} g^{-1}	Li et al. [46]
20.	Petroleum hydrocarbons in soil	Carbon mesh	Air	Soil MFC	–	Total charge generation: 79–86%	Li et al. [47]
21.	Petroleum hydrocarbon-contaminated soil	Graphite brush	Platinum coated carbon cloth	Soil-based MFC	Electrochemically active bacteria	Total dissolved solids (12.08% removal) and sulfates (62.64% removal)	Mohanakrishna et al. [64, 65]
22.	Polyaromatic hydrocarbon (PAH)	Graphite felt	Graphite felt	Single chamber plant-microbial fuel cell	117.3 mV	Removal: 48.04%	Zhao et al. [118]

(continued)

Table 2 (continued)

S.No	Petroleum products	Anode	Cathode	Reactor configuration	Power density	Treatment efficiency	References
23.	Petroleum hydrocarbon-contaminated soil	Plain graphite based plates	Plain graphite based plates	Soil based MFC	Acetate: 1126 (mW/m^2) Sewage: 1145 (mW/m^2)	*TPH degradation*: Acetate: 525 mg/L, 67.4% Sewage: 560 mg/L, 71.8% COD reduction Acetate: 72.1% Sewage: 74.6% *Sulfates removal* Acetate: 62.9% Sewage: 72.6%	Mohanakrishna et al. [63]
24.	Hydrocarbon-contaminated soil	Phenanthrene-coated bioanode	Pt coated carbon cloth	Dual chamber MFC	0.019 (mW/m^2)	Degradation of phenanthrene: 2 mg/cm^2 Power production: 37 (mW/m^2)	Sharma et al. [90]

TPH: Total petroleum hydrocarbon; COD: Chemical oxygen demand; SCOD: Soluble Chemical oxygen demand; TCOD: Total Chemical oxygen demand; LOI: Loss on ignition; ROOM: Readily oxidizable organic matter; AVS: Acid volatile sulfide

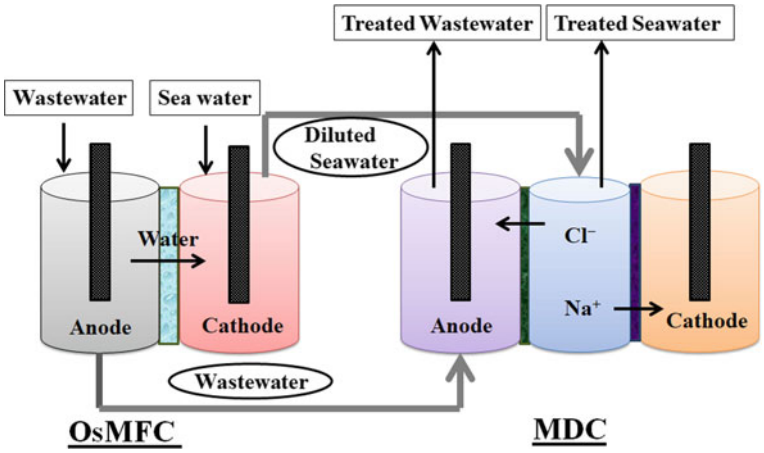

Fig. 4 Schematic representation of the dual system of hydraulically connected Osmotic MFC and MDC. Adapted from [88]

45,000 mg L^{-1} COD. Produced water (PW) refers to the large quantity of wastewater generated during oil and gas extraction. PW is usually characterized by high amounts of dissolved solids (TDS) and residual petroleum hydrocarbons, which are considerably hazardous to the environment. The level of environmental damage is dependent on the geographical location, age of the well, nature of geological formations at the specific location, the type of hydrocarbon products found the well and the stage of oil extraction. The bioelectrochemical treatment of PW was studied by Mohanakrishna et al. [64, 65] in two configurations viz., single- and dual-chamber microbial fuel cells (MFCs), of which the latter configuration displayed superior function with respect to power generation (1089 mW/m^2) and substrate degradation (COD removal efficiency = 60.2%) compared with the single-chamber configuration (PD 789 mW/m^2; COD removal efficiency = 54.7%); However, since the nature of PW varies based on the location and oil extraction stage, intensive studies are required to develop suitable processes with reference to the operating conditions; further, understanding the microbiology in connection with the composition of PW is also essential.

2.1.3 Microorganisms for PAH Treatment in Fuel Cells

A summary of the different microbial species employed in MFC operation for specific PAH substrates and their possible performance parameters are given in Table 3.

The hydrocarbon-degrading bacterial strain *Alcanivorax* has been shown to simultaneously improve bioelectricity generation and bioremediation performance in soil MFCs [42]. Li et al. [44, 45] suggested that employing the *Alcanivorax* strain is an

Table 3 Microbes involved in bioremediation of PAHs in MFC

S.No	Petroleum products	Reactor configuration	Biocatalyst	Power density	Treatment efficiency	References
1.	Refinery waste water	Dual Chambered MFC with aerated cathode	*Paenibacillus sp and Deinococcus sp*	102.93 mW/m^3	Oil removal rate: 85.56 ± 1.10%	Guo et al. [21]
2.	Oil refinery waste water	Single chamber with air-cathode	*Pseudomonas Putida*	0.005 mW/m^3	COD 30%	Majumder et al. [55]
3.	Hydrocarbon-contaminated soil	Soil tubular BES	*Comamonas testosteroni*, *Pseudomonas putida*, and *ochrobactrum anthropic*	39.1 (mW/m^2)	TPH removal: 78.7%	Lu et al. [53]
4.	Hydrocarbon-contaminated groundwater	Dual-chambered MFC	*Shewanella oneidensis* MR1 14,063, *Pseudomonas aeruginosa* NCTC 10,662 and mixed cultures	1.25 (mW/m^2)	COD: 65.6%	Adelaja et al. [2]
5.	Petroleum hydrocarbon soil	Soil MFC	Exoelectrogenes (*Geobacteraceae* sp., *Escherichia* sp.)	37 (mW/m^2)	TPH: 120%	Li et al. [41]
6.	Petroleum hydrocarbon-contaminated soil	Soil MFC	*Alcanivorax*	–	Degradation of petroleum hydrocarbons (PH) upto 268%	Li et al. [42]
7.	Petroleum Hydrocarbons	Soil MFC	*Alcanivorax*	43 (mW/m^2)	–	Li et al. [44, 45]
8.	Petroleum hydrocarbon-contaminated soil	Dual chamber MFC	*Geobacter* sp. and *Ochrobactrum* sp	220 (mW/m^2)	–	Zhou et al. [120]

(continued)

Table 3 (continued)

S.No	Petroleum products	Reactor configuration	Biocatalyst	Power density	Treatment efficiency	References
9.	Petroleum hydrocarbon-contaminated soil	Soil MFC	δ-Proteobacteria (Proteobacteria), Flavobacteria (*Bacteroidetes*) or *Clostridia* (*Firmicutes*)	304 (mA/m^2)	Degradation rate: 484%	Li et al. [44, 45]
10.	2,4-dichlorophenol	Dual chamber MFC	Mixed bacterial consortia (*Arcobacter*, *Cloacibacterium* and *Bacillus* sp.)	37 (mW/m^2)	COD: 41%	Hassan et al. [22]
11.	Petroleum hydrocarbon-contaminated aged soil	Soil MFC	*Proteobacteria*, *Firmicutes*, *Bacteroidetes*, *Actinobacteria*, *Chloroflexi*, *Planctomycetes* and *Acidobacteria*	153.8 ± 0.1 mA m^{-2}	bioelectricity generation rate: 0.321 C d^{-1} g^{-1}	Li et al. [46]
12.	Petrochemical wastewater	Dual chamber MFC	*Pseudomonas* spp. and *Bacillus* spp. Along with methanogenic archea *Methanobacterium* spp	850 (mW/m^2)	COD: 40%	Sarmin et al. [87]
13.	Hydrocarbon-contaminated soil	Dual chamber MFC	*Pseudomonas*, *Rhodococcus*, *Thauera* and *Ralstonia*	0.019 (mW/m^2)	Degradation of phenanthrene: 2 mg/cm^2 Power production: 37 (mW/m^2)	Sarmin et al. [90]

effective approach to eliminate soil contamination in barren areas/extreme environments. Hassan et al. [22] found that various exoelectrogens, including *Arcobacter*, *Aeromonas*, *Pseudomonas*, *Acinetobacter*, *Cloacibacterium*, and *Shewanella* sp., were involved in the degradation of 2, 4-DCP (dichlorophenol). This study discovered that *Cloacibacterium* sp. can degrade phenol in MFCs. Sarmin et al. [87] utilized pre-acclimatized mixed culture inoculum composed of electrogenic genera, such as *Bacillus* sp., *Pseudomonas* sp., and *Methanobacterium* sp. (methanogenic archaea), as biocatalysts in treating petrochemical wastewater (PCW) from an acrylic acid plant. This suggests that MFCs could be potential alternatives to conventional aerobic and anerobic processes, which are high energy-intensive.

2.1.4 Influence of Co-substrates and pH in MFCs for PAHs Degradation

The cultivation medium used for microbial consortia in MFC systems generally contains co-substrates to drive microbial growth during operation. Most studies have reported the use of co-substrates along with petroleum refinery wastewater in the anode chamber [22, 24, 44, 45, 66, 114, 116, 118]. In addition [60–62], used acetate as a co-substrate and it can be inferred that the substrate can stabilize microbial activity in an anode and continue electricity output at a steady current density level. pH is a crucial factor for anaerobic processes and serves as an intrinsic index of the changes in biological systems. Srikanth et al. explained that in batch mode operation, a change in pH toward the acidic range (pH < 4.0) [94] can be attributed to the competing action of mixed consortia in the redox reactions. Mohanakrishna et al. [60–62] reported that a single-chamber air-cathode MFC operated with PRW as the anolyte showed negligible change in the pH of the effluent. However [113], explained that the pH of all sediments slightly decreased, probably due to the fermentation of organics. Mohan and Chandrasekhar [59] Mohan & Chandrasekhar et al., demonstrated that the system pH was strongly controlled by the microbial metabolic rate, bioavailability, and mass transfer. In soil MFCs, the depletion of existing organic acids and the formation of bicarbonate salts leads to an increase in soil pH [26]. Li et al. [42] showed that pH values of the soil effectively correlated with the addition of sand as vast pH shifts were observed with increasing sand quantities. Li et al. [44, 45] elucidated that the addition of glucose substrate can neutralize soil pH and improve conductivity, and then the glucose is partly metabolized to organic acids (such as acetate). Soil pH and conductivity were the prominent factors that controlled the polyphenol oxidase and dehydrogenase activities, thus increasing TPH degradation and power output.

3 MFC for Dyes Degradation

Dyes containing one or more azo bonds are widely used in textile, leather, plastics, cosmetics, and food industries [74]. The color of these dyes is due to the azo bond and associated chromophores; so, the disposal of these dyes into the surface water not only affects the aesthetics, but their breakdown products have often been found to be carcinogenic, mutagenic, or toxic for humans [18]. These dyes can also obstruct the light and oxygen penetration into water, thus affecting the aquatic life. Several methods for the treatment of dye-containing wastewater which broadly fall into three categories: physical (adsorption, coagulation/flocculation, membrane filtration etc.), chemical (chemical oxidation, photo-catalytic oxidation, electrolysis, Fenton reagent etc.), and biological (biosorption, enzymatic degradation etc.) [34]. These physicochemical methods can be quite effective for color removal, but they have inherent disadvantages, including high operational costs and the generation of huge quantities of sludge for disposal. Recently, attempts have been made to address this issue through the biological route, using specific microorganisms for the cleaving of the azo bond. The biological treatment for the decolorization and degradation of azo dyes may be either aerobic, anaerobic, or a combination of both, depending on the type of microorganisms being employed [5, 35]. Most of the azo dyes are decolorized under anaerobic conditions however the anaerobic reduction is generally very slow, and produce methane rich gas. In most cases, the aromatic amines derived from azo dyes are not degraded under anaerobic conditions due to its high redox potential. These product amines released from azo dye decomposition are known, or suspected, to be more carcinogenic for humans [81] than the parent compound azo dyes. Thus, MFC has been employed for performing the dual duty of degrading the textile dyes and generating power. Moreover, such a system can reduce solids generation by 50–90% and reduce the load on their disposal. Based on their structure, dyes are classified into: acid/basic dyes, direct dyes, azo dyes, sulfur dyes, fiber reactive mordant dyes, etc., [38]. Dye molecule consists of two parts: (1) chromophores, which are functional groups of dyes, and (2) auxochromes, which enhance the color. Azo dyes account for more than 70% in the textile effluent. Most of the studies have focused the dye decolorization in the anode of MFC and few reports on dye decolorization in the cathode [27].

3.1 Azo Dye Decolorization and Degradation in the Anode

The co metabolism reaction is probably the main mechanism of dye degradation at the anode in which the reducing equivalents (electrons) are formed during the anaerobic oxidation of co-substrate. Once the substrate was oxidized and transferring the some portion of electrons for the exoelectrogens accumulated on the anode that pass through an external circuit producing current. Simultaneously, the other part of the electrons transferred to split the −N=N− bond in the azo dyes to form

aromatic amines in the anode chamber. Hence, there will be a competition for electrons between dye substances and an anode in an MFC. Different dyes were tested as anolyte with different substrates in MFC as shown in Table 4.

Electricity generation from glucose as co-substrate accompanied by decolorization of azo dye active brilliant red X-3B (ABRX3)was investigated by Sun et al. [97] using a microfiltration membrane air-cathode single-chamber microbial fuel cell (MFC). Around 90% of the dye was removed within 12 h at an dye concentration of 100 mg/l. The dye degradation mechanism via MFC technology as shown in Fig. 5. Anaerobic-aerobic sequential MFC reactor couple system was developed for Congo red degradation [48].

It was observed that the amines are formed in the anode chamber, and they are resistant to further degradation in the MFC under an anaerobic environment. To overcome this, a novel aerobic biocathode was designed by Sun et al. [95], since these intermediates are transferred to the cathodic chamber and further biodegradation takes place under aerobic conditions. Degraded intermediates transferred to the biocathode resulted in an almost 150% increase in open cycle potential (OCP) of the cathode accompanied by a 73% increase in stable voltage output from 0.33 to 0.57 V and a 300% increase in maximum power density from 50.74 to 213.93 mW/m^2. Azo dyes removal in CW has been investigated by Noonpui and Thiravetyan [73] and they demonstrated that a maximum 97% of dye removal in the constructed wetland (MFCCW); however, the removal efficiency was found to be a function of structure and size of the dye molecule. Moreover, they emphasized that the plant, soil, and microorganisms might all influence the efficiency of dye removal in a CW.

Double chambered MFCs are the most common design in MFCs studies which separated by a PEM. The protons transfer through PEM can be a limiting factor due to the suspended solids and soluble contaminants [28]. Moreover, double chambered MFC is difficult to scale-up. Single chambered up-flow membrane-less microbial fuel cell (UFML MFC) was developed by Thung et al. [100] for decolorization of Acid Orange 7 (AO7) and electricity generation simultaneously. Azo bond and naphthalene moieties were completely degraded but aromatic amines were remained in the effluent and however the COD and color removal by the bioreactor was up to 90%. The azo dyes (methyl orange (MO), Congo red (CR), reactive yellow (RY), reactive red (RR), along with nutrient medium were tested as anolytes in the *Pseudomonas-catalyzed* MFC at an external resistance of 220 Ω [29]. In the anode chamber maintained under anaerobic conditions more than 90% of MO and RB could be decolorized by *P. aeruginosa* in 5 d, but RR was decolorized only about 74%. Generally, the microorganisms produce azoreductases which reductively cleave the highly electrophilic azo bond at the expense of a reducing agent, typically NAD(P)H [54]. It is expected that reduction under anaerobic environments will be nonspecific, although the rate of decolorization depends on the organic source and the dye structure (Engineering 2012). It suggested that a simple structure and low-molecular weight azo dye MO degraded faster in MFC than CR, RR, and RY which are highly substituted and of high molecular weight. On the other hand, it was also observed that bacterial decolorization of di azo RB was more superficial when compared with either of the mono azo dyes (RR, RY). The presence of two electron withdrawing group (SO_3^{-1}) at

Table 4 Different dyes for anolyte with different substrates in MFC

S.No	Dye	Anode	Cathode	Co-substrate	Bio-catalyst	Power density	Decolourization efficiency	References
1.	Active brilliant red X-3B	Porous carbon papers	Porous carbon papers with Pt and PTFE	Glucose	Anaerobic sludge	234 mW/m^2	90%	Sun et al. [97]
2.	Methylene blue	Bottom of microcam	Rhizopheric zone-wetland	Sucrose	Wastewater	15.7mW/m^2	80%	Yadav et al. [108]
3.	Reactive Brilliant red X-3B	Granular activate carbon	SS mesh	Glucose	Anaerobic sludge	302mW/m^3	91.24%	Fang et al. [13]
4.	Reactive Brilliant red X-3B	Activated carbon/SS mesh	Activated carbon/SS Mesh	Glucose	Wastewater	852mW/m^3	94.9%	Fang et al. [14]
5.	Methyl orange	Granular activate carbon	Granular activated carbon	Glucose	Synthetic wastewater	688 mW/m^3	75–85%	Fang et al. [15]
6.	Congo red	Porous carbon papers	Porous carbon papers	Glucose	*Pseudomonas sp.* and *Aquamicrobium sp*	29 mW/m^2	20.3% increase	Sun et al. [96]
7.	Congo red	Graphite felt	Graphite felt	Glucose	Anaerobic sludge	0.193 ± 0.0023	70%	Huang et al. [26]
8.	Mordant orange	Toray carbon paper(TCP)	Toray carbon paper(TCP)	Acetate	Bacterial culture	4.9 ± 0.5 Wm^{-3}	89%	Sarma et al. [86]
9.	Acid red(18)	Carbon felt	Carbon felt	Acetate	Mixed consortium	8.67mW/m^2	91%	Oon et al. [75]

(continued)

Table 4 (continued)

S.No	Dye	Anode	Cathode	Co-substrate	Bio-catalyst	Power density	Decolourization efficiency	References
10.	Brilliant green	SS mesh-GO	SS mesh-GO	Glucose	*Geobactor sulfureducens*	0.04 mW/cm^2	80%	Khalid et al. [36]
11.	Methyl orange	Carbon felt	Carbon felt	Acetate	*Proteobacteria, Actinobacteria, Bacteroidetes, Planctomycetes, Firmicutes*	628 mW/m^2	92.5%	Zhong et al. [119]
12.	Acid red (18) Acid orange(7) Congo red	Carbon felt	Carbon felt	Acetate	Mixed consortium	1.58 mW/m^2 1.13 mW/m^2 1.02 mW/m^2	96% 67% 60%	Oon et al. [77]
13.	Methyl red	Carbon cloth	Platinum rod	Glucose	Bacterial consortium	–	71.7%	Krithika et al. [37]
14.	Sunset yellow	Graphite rod	Graphite rod	Acetate	Mixed consortium	46.42 ± 0.01	93%	Tacas et al. [98]

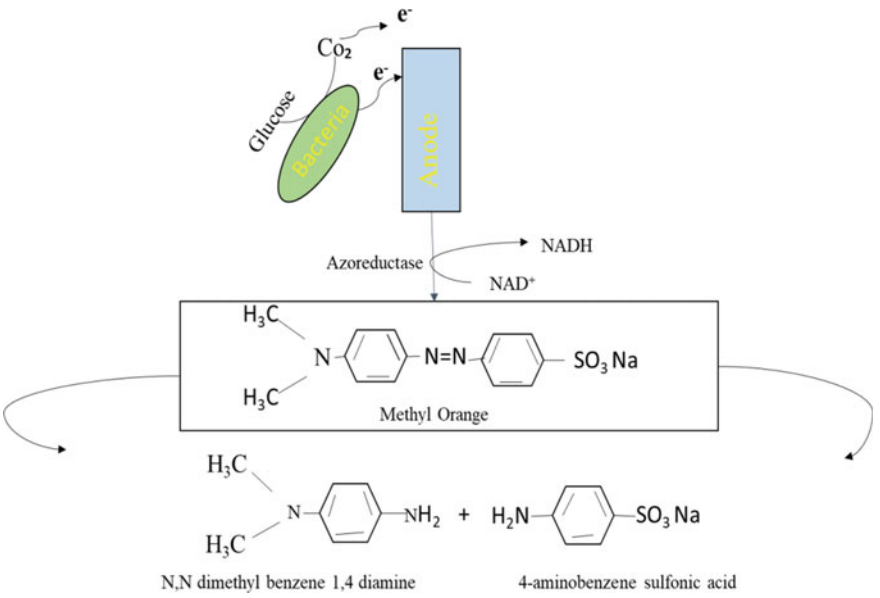

Fig. 5 Degradation mechanism of dye

ortho position to azo bonds and OH group of the naphthol ring in RB were also the main aspect of the azo bond cleavage. The sulfo groups could withdraw electrons from azo bond by resonance, and the environment in the proximity of azo bond could become more electrophilic for decolorization [115].

Reduction of azo dye in the anode chamber might be performed either by direct enzymatic reaction or mediated reaction of enzyme cofactors, which are biologically regenerated by sulfate-reduction bacteria (SRB) to break down the azo bond [85]. Santos et al. [11] used single-chamber air-cathode microbial fuel cells to investigate the interaction mechanisms among Congo red decolorization, sulfide oxidation, and bioelectricity generation. The results showed that effective removal of sulfide (98%) and azo dyes (88%) was achieved at an initial sulfide/dye ratio of 0.9 under neutral conditions, accompanied by a maximum power output of approximately 23.50 mWm^{-2}.

3.2 Azo Dye Decolorization and Degradation in the Cathode

The color of dyes is due to azo bond and associated chromophores, so disposal of dyes into surface water not only affects the aesthetic but cause also biotoxicity. The azo dye was used in the cathode with the dual objective of solving as facilitator for electron acceptor and the possibility of decolorization. The cathode chamber was continuously sparged with N_2 gas to avoid O_2 competition with the azo dyes for

electrons. The reduction reactions in the cathode chamber are described by Goyal and Minocha [20], Menek, Zeyrekl, and Karaman n.d.; Parthasarathy and Narayanan [78] in which the –N=N– double bond was reduced to hydrazo (1) or amine (2), via the consumption of two or four electrons.

$$-\mathrm{N{=}N}- + 2\mathrm{e} + 2\mathrm{H}^{+} \rightarrow -\mathrm{NH} - \mathrm{NH}- \quad (1)$$

$$-\mathrm{N{=}N}- + 4\mathrm{e} + 4\mathrm{H}^{+} \rightarrow -\mathrm{NH_2} - \mathrm{NH_2}- \quad (2)$$

Mu et al. [68] achieved an effective decolorization rate of dye was 2.64 ± 0.03 mol m^{-3} d^{-1} achieved at the cathode of a bioelectrochemical system while acetate was used in the anode [68]. Reduction of azo dyes in the cathode of MFC using electrons produced from metabolic oxidation of *Klebsiella pneumoniae* strain L17 in the anode [50]. Different azo dyes congo red, methyl orange and reactive blue, were tested as catholyte in *Pseudomonas-catalyzed* MFC using a graphite block [29]. Compared to potassium ferricyanide (72.8 ± 17.8 μW/m^2) and potassium permanganate (86.28 ± 16.8), addition of azo dyes enhanced the power output by several fold (congo red-91.73 ± 21.2; Methyl orange 314.07 ± 22.6; Reactive blue 172 294.43 ± 11.9 μW/m^2). Lot of research findings (Table 5), the degradation efficiency was high; however it was found that low power density resulting from the small specific capacitance of the carbon-based materials.

3.3 *Key Parameters Influencing the MFC for Dyes Degradation*

Developing an MFC for dye waste water treatment with a simple configuration at affordable costs for the ease of scale-up still remains the challenge. Many workers have reported that the several factors that affect the MFC performance including the microbes, the proton selective membrane, the material of the electrodes, the cathode/anode catalyst, the electrode spacing, and the system design [31]. It is known that electron transfer between the electron carriers in the bacteria transport chain and the anode/cathode is low, leading to a high internal resistance that reduces the power generated in MFCs.

3.3.1 Effect of Co-substrate

One of the most crucial aspects of MFC is the substrates used due to their effect on the dye degradation and power output. A report by [97], when confectionary and glucose wastewater were utilized as co-substrates in MFC along with a model azo dye, there

Table 5 Different dyes for catholyte with a different substrate in MFC

S.No	Dye	Anode	Cathode	Substrate	Bio-catalyst	Power density	Decolourization efficiency	References
1.	Methyl orange	Carbon felt	Carbon felt	Glucose	*K. pneumoniae strain L17*	34.77 mW/m^{-2}	90%	Liu et al. (2009)
2.	Congo red	Rough plain carbon felt	Carbon felt	Glucose	Anaerobic sludge	364.5 mW/m^{-2}	80%	Li et al. [48]
3.	Reactive blue 221	Graphite bars	Graphite bars	Urea	Anaerobic sludge	27 mW/m^{-2}	83%	Bakhshian et al. (2011)
4.	Active brilliant red X-3B	Porous carbon papers	Porous carbon papers	Glucose	Domestic wastewater	50.74 mW/m^2 to 213.93 mW/m^2	90%	Sun et al. [95]
5.	Acid Orange 7	Carbon plate	Carbon felt	Sodium acetate	Anaerobic sludge	7.07 mW/m^{-2}	96%	Thung et al. [100]
6.	Reactive Brilliant red X-3B	Granular activated Carbon	Granular activated Carbon	Glucose	Wastewater	117mW/m^3	92%	Fang et al. [16]
7.	Acid orange 7	Carbon felt	Carbon cloth	Solidified gel	Ganoderma lucidum BCRC 36,123	13.38 mW/m^2	90%	Lai et al. [40
8.	Orange II	Carbon cloth	Carbon paper	Sodium acetate	Wastewater	72.6 mW m^{-2}	96.3%	Xu et al. [106]
9.	New coccine, Acid orange 7, Reactive red 120 and Reactive green 19	Carbon felt	Carbon felt	Sodium acetate	Wastewater	20.64 mW/m^2	95.1 ± 1.1%	Oon et al. [76]

(continued)

Table 5 (continued)

S.No	Dye	Anode	Cathode	Substrate	Bio-catalyst	Power density	Decolourization efficiency	References
10.	Methyle Orange	Graphite	Graphite	Glucose	*P.aeruginosa*	95.83 ± 4.10 $\mu W/m^2$	87 ± 2.8	Narayanasamy and Jayaprakash [69]
11.	Methyl orange	Carbon felt	Carbon felt	Glucose	Anaerobic sludge	502.5 ± 17.1 mW/m^2	97.1 ± 1.8%	Liang et al. [49]
12.	Orange II	Carbon cloth	Carbon paper	Acetate	Anaerobic sludge	206.2 ± 3.1 mW m^2	80%	Xu et al. [107]
13.	Congo red	Graphite fiber brush	Carbon cloth	Acetate	Anaerobic sludge	23.50 mW/m^2	98%	Dai et al. [11]

is a competition between the anode and azo dye reduction for electrons from co-substrate oxidation. Bioelectricity generation with a simultaneous Congo red degradation can be achieved using glucose, acetate sodium, and ethanol as co-substrate in PEM air-cathode single-chamber MFC. More than 98% of the Congo red (300 mg/L) was decolorized within 36 h for all tested co-substrates during the electricity generation. Glucose produced the highest power densities when compared to Ethanol [6, 57] studied that simultaneous electricity generation and tetra-azo dye (Direct Red 80) decolorization was examined in a dual-chamber MFC. Glucose was identified as a better co-substrate than acetic, propionic, and lactic acid for dye removal and current production (477.8 mW/m^2). It can be understood that the low-molecular co-substrates can be easily degraded, excessive co-substrate addition can lead to high COD, in addition to resource (dye) waste. Anaerobic azo dyes degradation in MFC are strongly influenced by co-substrate type and its concentration suggested that the combination of dye containing waste water and high organic content waste water from food/biorefinery industries that is easily biodegraded simultaneously that can both improve cost and energy.

3.3.2 Effect of PH

Anodic pH microenvironment is one of the important factors which can influence substrate metabolic activity and as well as proton transfer mechanism [80]. pH has a significant factor on dye degradation efficiency because of enzymatic activity depends on the pH. The color of the solution and solubility of the dyes is affected by the pH. The release of metabolic products by a biocatalyst into the anolyte will lower the system pH [31] acidic can bring about alterations in several MFC system parameters such as concentration of ions, membrane potential, proton motive force and adversely affect bacterial growth and adhesion during MFC operation. Raghavulu et al. [80] found that acidophilic pH in anodic chamber was effective performance with respect to power output compared to the corresponding neutral and alkaline operations. However, substrate degradation was observed to be higher in neutral condition followed by alkaline and acidophilic operations. On the other side, though cation exchange membranes (CEM) and anion exchange membranes (AEM) are less expensive separators [72], pH in the cathode chamber increases because of the transport of the cationic species other than protons (particularly of alkali and alkaline earth metals) through the CEM. This increase in pH negatively impacts the performance of the MFC. For every 3 unit increase in pH, a loss of potential of 0.18 V occurs in the cathode, according to [83]. Ideally, the only membranes that can prevent the pH effect on MFC performance are 100% proton selective membrane. Buffers have been commonly used in MFCs in order to (i) maintain a suitable pH for the anodic bacteria biofilm, (ii) increase solution conductivity, (iii) increase the transfer of protons generated at the anode to the cathode, and (iv) reduce the operational pH, which would be beneficial for oxygen reduction. Hence, the primary challenge in scaling-up an MFC application is to ensure a more stable electrolyte environment in the MFC by adding buffers in continuous mode.

3.3.3 Effect of Hydraulic Retention Time (HRT)

HRT is the average amount of time that reactants stay in a reactor and it is calculated by dividing the volume of a reactor by the influent flow rate. Oon et al. [75] studied the effect of HRT on MFC performance and reported that longer HRT allows longer contact time between the substrates and biofilm, which enabled more organic matter to be oxidized by microbes, thus, led to a higher reduction of COD. It was found that the COD removal efficiency at 1 day HRT was 70%, and rose about 7% when MFC operation was extended to 2 days HRT and it also enhanced the azo dye decolorisation and bioelectricity generation.

Oon et al. [75] studied the influence of HRT on the decolorisation and bioelectricity generation can be improved by longer HRT (2 days) and by regulating the external resistance closer to the internal resistance of the MFC system. The low concentration of New Coccine (NC) (25 mg/L) improved 17% of the power density to 20.13 ± 0.37 W/m^3. The internal resistance decreased from 50 to 32 Ω. As dye concentration increases, the decolorisation efficiency maintained over 90% (200 mg/L NC), whereas, power density dropped to 10.83 ± 1.21 W/m^3. Results showed that both decolorisation and power performances were improved with 2 days HRT. However, the HRT was too high, then the depletion of substrate occurs. Due to mass transfer losses, it increased the overpotential of the system thereby reducing the power output. Li et al. [48] studied the influence of HRT on the power density. The maximum power density reached 552.2 mW/m^2, when the HRT was 14.8 h. Increasing HRT from 14.8 to 44.4 h decreased the substrate concentration in the anodic chamber, which increased the open circuit voltage of anode from −431 to −283.8 mV. Longer HRTs reduce the organic loading rate, thereby reducing the cell performance due to the rapid depletion of the substrate, whereas shorter HRTs favor the development of non-exoelectrogenous bacteria, which reduces the CE and electrochemical performance with less effective COD removal, hence optimum HRT is preferred.

3.3.4 Microorganisms in Fuel Cells for Dye Wastewater Treatment

Many dissimilatory metal reducing bacteria possess the ability to transfer electrons directly attracting much attention for the application of MFC in dye degradation. Pure strain such as Proteus hauseri ZMd44 [8] and *Pseudomonas aeruginosa* [31] has been shown to generate electricity in mediator-less MFC systems and degrade the dyes simultaneously. Different azo dyes such as methyl orange (MO), Congo red, reactive blue 172 (RB), reactive yellow 145, and reactive red 2 were investigated in the *Pseudomonas*-catalyzed MFC [29], which is capable of producing pyocyanin and several other electron-shuttling compounds. Several isolates such as *Geobacter sulfurreducens* and *Beta Proteobacteria* have also been shown to produce energy output without the addition of mediators in MFC and dye removal [13]. In some cases, interestingly it has been found that the decolorized intermediates of azo dyes are redox-active chemical species which itself act as a mediator [8].

An overview of different species of microorganisms employed in the MFC operation with specified dye-bearing substrate. Different species involved in the MFC operation and their possible decolorization efficiency with power output is given in Table 4. Bacteria were identified as the members of the genera *Azospirillum*, *Methylobacterium*, *Rhodobacter*, *Desulfovibrio*, *Trichococcus*, and *Bacteroides* were more abundant in the dye degradation process.

3.3.5 Effect of Electrode

Among all the MFC components, the electrode materials play a crucial role in power generation since the cost of the electrode is a key barrier to the translation of MFCs from the laboratory scale to the industrial process [82]. The anodic material must be conductive, highly porous with enhanced active surface area, noncorrosive, and exhibit redox behavior compatible with microbial metabolism [30]. Different types of materials ranging from non-corrosive stainless steel to versatile carbons have been examined as anodes in different configurations [78]. Similarly, cathode materials also have an equally important effect on MFC operation and productivity. Ideally, cathodes are expected to have a high redox potential to accept electrons [71]. However, it is difficult to obtain high cathodic potentials unless metal-oxide-loaded catalysts are used. [33] employed granular activated carbon as the bioanode and biocathode for the treatment of industrial dye wastewater in an MFC to avoid the platinum catalyst and Nafion membrane, which are two tailbacks in MFC in terms of affordable costs. A stable voltage of 0.214 V was attained with 73% and 77% decolorization at the anode and cathode, respectively. Cui et al. [10] filled a cuboid titanium basket (L 13 cm × W 10 cm × H 7 cm) tightly with granular graphite and welded a titanium rod of 30 cm length on the basket for the external circuit connection. The large specific surface area provided by the graphite granules in this configuration was appreciably better for the power generation. Graphite-epoxy resin composite electrodes (MS-GECE) doped with various metal salts (MS) were tested by Jayapriya and Ramamurthy [31, 32] in dye degradation using *Pseudomonas aeruginosa* as the biocatalyst. The best-performing MFC was the one with Mn^{2+} GECE electrodes, producing the highest power density for methyl orange (4676 mW/m^2) and reactive black (2593 mW/m^2).[96] used a biocathode MFC for Congo red decolorization in textile dyeing sludge. The biocathode MFC exhibited excellent performance, achieving Congo red decolorization rapidly in 48 h, with a power density of 9 mW/m^2. Bulk-modified graphite-polyester composite electrodes (GPECE) doped with metal salts (MS-GPECE) prepared by casting [69] displayed redox behavior suitable for bacterial metabolism, and enhanced biofilm formation was observed in a Pseudomonas-catalyzed microbial fuel cell (MFC). The highest power density (1575 ± 223.26 $\mu W/m^2$) achieved with Ni-GPECE as the cathode material was approximately 15-fold higher than that obtained with graphite block, and its methyl-orange decolorization efficiency was 97 ± 1.4%. Nickel cobaltite ($NiCo_2O_4$)- and conductive polyaniline (PANI)-modified carbon cloth (CC) electrodes were synthesized by simple, low-cost hydrothermal and electropolymerization techniques, respectively,

by Narayanasamy and Jayaprakash [70]. Among the different electrode combinations tested, the surface-modified electrode Ni/PANI/CC (NCCP) produced the maximum power density when applied as a cathode (12.194 ± 0.59 mW/m^2), which was 15.9-fold higher than that obtained with CC (0.769 ± 0.0023 mW/m^2), besides a high decolorization efficiency of $80.5 \pm 2.1\%$. The preferred electrodes for dye decolorization seem to be mostly carbon and graphite electrodes. Though the maximum color removal has been achieved with carbon-based electrodes in combination with a Pt-catalyst-modified cathode, the incorporation of carbon nanotubes (CNTs) in conductive polymers has become a promising cost-effective electrode fabrication strategy in the MFC arena [72, 99]. All these efforts aspire to unearth the best electrode combination for effective decolorization of azo dyes while generating power as a by-product in MFCs.

4 Conclusion

If power output in these systems can be increased, MFC technology may provide a novel method to offset the high operating cost of traditional wastewater treatment plants, thereby making water recycling and waste disposal more inexpensive for developing and developed nations. MFCs operated with different synthetic dyes and polycyclic aromatic compounds at the pilot-scale demonstrate feasibility but require technical improvements toward high degradation efficiency and lower cost to be economically competitive at the industrial level. Evident inadequacies in commercialization aspects, including cost and durability, have been detected with respect to some MFC components, such as electrode materials, oxygen-reduction reaction catalysts, and membranes. Nowadays, attention toward the development of alternate materials is mounting, and MFC technology might lay a sophisticated path for the direct management of industrial dye effluents and PAH-rich petroleum waste via bioremediation.

References

1. Abbasian F, Lockington R, Mallavarapu M, Naidu R (2015) A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria. Appl Biochem Biotechnol 176(3):670–699
2. Adelaja O, Keshavarz T, Kyazze G (2014) Enhanced biodegradation of phenanthrene using different inoculum types in a microbial fuel cell. Eng Life Sci 14(2):218–228
3. Adelaja O, Keshavarz T, Kyazze G (2015) The effect of salinity, redox mediators and temperature on anaerobic biodegradation of petroleum hydrocarbons in microbial fuel cells. J Hazard Mater 283:211–217
4. Bregnard T-A, Höhener P, Zeyer J (1998) Bioavailability and biodegradation of weathered diesel fuel in aquifer material under denitrifying conditions. Environ Toxicol Chem 17(7):1222–1229
5. Buitrón G, Quezada M, Moreno G (2004) Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter. Biores Technol 92(2):143–149

6. Cao Y, Yongyou H, Sun J, Hou B (2010) Explore various co-substrates for simultaneous electricity generation and congo red degradation in air-cathode single-chamber microbial fuel cell. Bioelectrochemistry 79(1):71–76
7. Chandrasekhar K, Venkata Mohan S (2012) Bio-electrochemical remediation of real field petroleum sludge as an electron donor with simultaneous power generation facilitates biotransformation of PAH: effect of substrate concentration. Biores Technol 110:517–525
8. Chen BY et al (2010) Assessment upon Azo dye decolorization and bioelectricity generation by proteus hauseri. Biores Technol 101(12):4737–4741
9. Coelho A, Castro AV, Dezotti M, Sant'Anna GL (2006) Treatment of petroleum refinery sourwater by advanced oxidation processes. J Hazard Mater 137(1):178–184
10. Cui D et al (2014) Enhanced decolorization of azo dye in a small pilot-scale anaerobic baffled reactor coupled with biocatalyzed electrolysis system (ABR-BES): a design suitable for scaling-up. Biores Technol 163:254–261
11. Dai Q et al (2020) Sulfide-mediated azo dye degradation and microbial community analysis in a single-chamber air-cathode microbial fuel cell. In: Bioelectrochemistry
12. Environmental Engineering (2012) Microbial degradation of xenobiotics. http://www.springerlink.com/index/10.1007/978-3-642-23789-8
13. Fang Z, Song HL, Cang N, Li XN (2013) Performance of microbial fuel cell coupled constructed wetland system for decolorization of azo dye and bioelectricity generation. Biores Technol 144:165–171
14. Fang Z, Song HL, Cang N, Li XN (2015) Electricity production from Azo dye wastewater using a microbial fuel cell coupled constructed wetland operating under different operating conditions. Biosens Bioelectron 68:135–141
15. Fang Z, Song H, Yu R, Li X (2016) A microbial fuel cell-coupled constructed wetland promotes degradation of azo dye decolorization products. Ecol Eng 94:455–463
16. Fang Z, Cao X, Li X, Wang H, Li X (2017) Electrode and azo dye decolorization performance in microbial-fuel-cellcoupled constructed wetlands with different electrode size during long-term wastewater treatment. Bioresour Technol 238: 450–460
17. Fu L et al (2019) Ozonation reactivity characteristics of dissolved organic matter in secondary petrochemical wastewater by single ozone, ozone/H_2O_2, and ozone/catalyst. Chemosphere 233:34–43
18. Ganesh R, Boardman GD, Michelsen D (1994) Fate of azo dyes in sludges. Water Res 28(6):1367–1376
19. Giannopoulos D et al (2007) Quantification of emissions from the co-incineration of cutting oil emulsions in cement plants—Part II: trace species. Fuel 86(16):2491–2501
20. Goyal RN, Minocha A (1985) Electrochemical behaviour of the bisazo dye, direct red-81. J Electro Chem 193(1–2):231–240
21. Guo X et al (2014) The influence of microbial synergistic and antagonistic effects on the performance of refinery wastewater microbial fuel cells. J Power Sour 251:229–236
22. Hassan H et al (2018) Microbial community and bioelectrochemical activities in MFC for degrading phenol and producing electricity: microbial consortia could make differences. Chem Eng J 332:647–657
23. Holzman DC (2005) Microbe power!. Environ Health Perspect 113(11)
24. Hosseinpour M et al (2016) Ethylene glycol biodegradation in microbial fuel cell. Energy Sour Part A: Recov Utiliz Environ Effects 38(8):1096–1102
25. Huang DY et al (2011) Enhanced anaerobic degradation of organic pollutants in a soil microbial fuel cell. Chem Eng J 172(2–3):647–653
26. Huang L et al (2011) Degradation of pentachlorophenol with the presence of fermentable and non-fermentable co-substrates in a microbial fuel cell. Biores Technol 102(19):8762–8768
27. Illamathi J (2017) Microbial fuel cells for dye decolorization. Environ Chem Lett 16(10)
28. Jang JK et al (2004) Construction and operation of a novel mediator- and membrane-less microbial fuel cell. Process Biochem 39(8):1007–1012
29. Jayaprakash J, Parthasarathy A, Viraraghavan R (2016) Decolorization and degradation of monoazo and diazo dyes in pseudomonas catalyzed microbial fuel cell. Environ Prog Sustain Energy 35(6):1623–1628

30. Jayapriya J et al (2012) Preparation and characterization of biocompatible carbon electrodes. Compos B Eng 43(3):1329–1335
31. Jayapriya J, Ramamurthy V (2012) Use of non-native phenazines to improve the performance of pseudomonas aeruginosa MTCC 2474 catalysed fuel cells. Biores Technol 124:23–28
32. Jayapriya J, Ramamurthy V (2014) The role of electrode material in capturing power generated in pseudomonas catalysed fuel cells. Can J Chem Eng 92(4):610–614
33. Kalathil S, Lee J, Cho MH (2011) Granular activated carbon based microbial fuel cell for simultaneous decolorization of real dye wastewater and electricity generation. New Biotechnol 29(1):32–37
34. Kaushik A, Singh A (2020) Metal removal and recovery using bioelectrochemical technology: the major determinants and opportunities for synchronic wastewater treatment and energy production. J Environ Manag, 270
35. Khalid A, Arshad M, Crowley DE (2009) Biodegradation potential of pure and mixed bacterial cultures for removal of 4-nitroaniline from textile dye wastewater. Water Res 43(4):1110–1116
36. Khalid S, Alvi F, Fatima M, Aslam M, Riaz S, Farooq R, Zhang Y (2018) Dye degradation and electricity generation using microbial fuel cell with graphene oxide modified anode. Mater Lett 220:272–276
37. Krithika T, Kavitha R, Dinesh M, Angayarkanni J (2021) Assessment of ligninolytic bacterial consortium for the degradation of azo dye with electricity generation in a dual-chambered microbial fuel cell. Environ Challenges 4
38. Kulkarni SV et al (1985) Textile dyes and dyeing equipment: classification, properties, and environmental aspects, i
39. Kumari S, Regar RK, Manickam N (2018) Improved polycyclic aromatic hydrocarbon degradation in a crude oil by individual and a consortium of bacteria. Biores Technol 254:174–179
40. Lai CY, Wu CH, Meng CT, Lin CW (2017) Decolorization of azo dye and generation of electricity by microbial fuel cell with laccase-producing white-rot fungus on cathode. Appl Energy 188:392–398
41. Li X et al (2014) Extended petroleum hydrocarbon bioremediation in saline soil using Pt-free multianodes microbial fuel cells. RSC Adv 4(104):59803–59808
42. Li X et al (2015) Sand Amendment enhances bioelectrochemical remediation of petroleum hydrocarbon contaminated soil. Chemosphere 141:62–70
43. Li X, Wang X, Zhao Q et al (2016) Carbon fiber enhanced bioelectricity generation in soil microbial fuel cells. Biosens Bioelectron 85:135–141
44. Li X, Wang X, Wan L et al (2016) Enhanced biodegradation of aged petroleum hydrocarbons in soils by glucose addition in microbial fuel cells. J Chem Technol Biotechnol 91(1):267–275
45. Li X, Wang X, Zhang Y et al (2016) Salinity and conductivity amendment of soil enhanced the bioelectrochemical degradation of petroleum hydrocarbons. Sci Rep 6(September):1–11
46. Li X et al (2018) Surfactants selectively reallocated the bacterial distribution in soil bioelectrochemical remediation of petroleum hydrocarbons. J Hazard Mater 344:23–32
47. Li X, Li Y, Zhang X et al (2019) Long-term effect of biochar amendment on the biodegradation of petroleum hydrocarbons in soil microbial fuel cells. Sci Total Environ 651:796–806
48. Li Z et al (2010) Azo dye treatment with simultaneous electricity production in an anaerobic-aerobic sequential reactor and microbial fuel cell coupled system. Biores Technol 101(12):4440–4445
49. Liang S, Zhang B, Shi J, Wang T, Zhang L, Wang Z, Chen C (2018) Improved decolorization of dye wastewater in an electrochemical system powered by microbial fuel cells and intensified by micro-electrolysis. Bioelectrochemistry 124:112–118
50. Liu XW et al (2011) Integration of a microbial fuel cell with activated sludge process for energy-saving wastewater treatment: taking a sequencing batch reactor as an example. Biotechnol Bioeng 108(6):1260–1267
51. Lovley DR (1993) Dissimilatory metal reduction. Annu Rev Microbiol 47:263–290
52. Lovley DR, Woodward JC, Chapelle FH (1996) Rapid anaerobic benzene oxidation with a variety of chelated Fe(III) forms. Appl Environ Microbiol 62(1):288–291

53. Lu L et al (2014) Microbial metabolism and community structure in response to bioelectrochemically enhanced remediation of petroleum hydrocarbon-contaminated soil. Environ Sci Technol 48(7):4021–4029
54. Maier J et al (2004) A New Alkali-thermostable azoreductase from bacillus sp. Strain SF. Appl Environ Microbiol 70(2):837–844
55. Majumder D et al (2014) Electricity generation and wastewater treatment of oil refinery in microbial fuel cells using pseudomonas putida. Int J Mol Sci 15(9):16772–16786
56. Menek N, Zeyrekl S, Karaman Y, Investigation of electrochemical behavior of mordant dye (C. I. 17135) at glassy carbon and silver electrodes 4(1):89–104
57. Miran W et al (2016) Simultaneous electricity production and direct red 80 degradation using a dual chamber microbial fuel cell. Desalin Water Treat 57(19):9051–9059
58. Mohammadi L et al (2020) Petroleum hydrocarbon removal fromwastewaters: a review. Processes 8(4):1–34
59. Mohan SV, Chandrasekhar K (2011) Self-induced bio-potential and graphite electron accepting conditions enhances petroleum sludge degradation in bio-electrochemical system with simultaneous power generation. Biores Technol 102(20):9532–9541
60. Mohanakrishna G et al (2018) Enhanced treatment of petroleum refinery wastewater by short-term applied voltage in single chamber microbial fuel cell. Biores Technol 253:16–21
61. Mohanakrishna G, Abu-Reesh IM, Al-Raoush RI (2018) Biological anodic oxidation and cathodic reduction reactions for improved bioelectrochemical treatment of petroleum refinery wastewater. J Clean Prod 190:44–52
62. Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM (2018) Induced bioelectrochemical metabolism for bioremediation of petroleum refinery wastewater: optimization of applied potential and flow of wastewater. Biores Technol 260:227–232
63. Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM (2020) Sewage enhanced bioelectrochemical degradation of petroleum hydrocarbons in soil environment through bioelectrostimulation. Biotechnol Rep, 27
64. Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM, Aljaml K (2019) Removal of petroleum hydrocarbons and sulfates from produced water using different bioelectrochemical reactor configurations. Sci Total Environ 665:820–827
65. Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM, Pant D (2019) A microbial fuel cell configured for the remediation of recalcitrant pollutants in soil environment. RSC Adv 9(71):41409–41418
66. Morris JM, Jin S (2008) Feasibility of using microbial fuel cell technology for bioremediation of hydrocarbons in groundwater. J Environ Sci Health—Part A Toxic/Hazard Subst Environ Eng 43(1):18–23
67. Morris JM, Jin S (2012) Enhanced biodegradation of hydrocarbon-contaminated sediments using microbial fuel cells. J Hazard Mater 213–214:474–477
68. Mu W et al (2009) 3-Phenyllactic acid production by substrate feeding and PH-control in fed-batch fermentation of lactobacillus Sp. SK007. Biores Technol 100(21):5226–5229
69. Narayanasamy S, Jayaprakash J (2018) Improved performance of pseudomonas aeruginosa catalyzed MFCs with graphite/polyester composite electrodes doped with metal ions for azo dye degradation. Chem Eng J 343:258–269
70. Narayanasamy S, Jayaprakash J (2021a) Carbon cloth/nickel cobaltite ($NiCo_2O_4$)/polyaniline (PANI) composite electrodes: preparation, characterization, and application in microbial fuel cells. Fuel, 301
71. Narayanasamy S, Jayaprakash J (2021b) Conducting polymers for electrocatalysts. In: Conducting polymers for advanced energy applications, pp 315–335
72. Navanietha KR, Yu JS (2015) Bioenergy: opportunities and challenges. In: Bioenergy: opportunities and challenges
73. Noonpui S, Thiravetyan P (2011) Treatment of reactive azo dye from textile wastewater by burhead (Echinodorus Cordifolius L.) in constructed wetland: effect of molecular size. J Environ Sci Health—Part A Toxic/Hazard Subst Environ Eng 46(7):709–714

74. O'Neill C et al (1999) Colour in textile effluents—Sources, measurement, discharge consents and simulation: a review. J Chem Technol Biotechnol 74(11):1009–1018
75. Oon YS et al (2018) Disclosing the synergistic mechanisms of azo dye degradation and bioelectricity generation in a microbial fuel cell. Chem Eng J 344:236–245
76. Oon YS, Ong SA, Ho LN, Wong YS, Oon YL, Lehl HK, Thung WE, Nordin N (2017) Microbial fuel cell operation using monoazo and diazo dyes as terminal electron acceptor for simultaneous decolourisation and bioelectricity generation. J Hazard Mater 325:170–177
77. Oon YL, Ong SA, Ho LN, Wong YS, Dahalan FA, Oon YS, Teoh TP, Lehl HK, Thung WE (2020) Constructed wetland–microbial fuel cell for azo dyes degradation and energy recovery: influence of molecular structure, kinetics, mechanisms and degradation pathways. Sci Total Environ 720
78. Parthasarathy P, Narayanan SK (2014) Effect of hydrothermal carbonization reaction parameters on. Environ Prog Sustain Energy 33(3):676–680
79. Priyadarshini M, Ahmad A, Das S, Ghangrekar MM (2021) Application of microbial electrochemical technologies for the treatment of petrochemical wastewater with concomitant valuable recovery: a review. Environ Sci Pollut Res
80. Raghavulu SV, Mohan SV, Goud RK, Sarma PN (2009) Effect of anodic PH microenvironment on microbial fuel cell (MFC) performance in concurrence with aerated and ferricyanide catholytes. Electrochem Commun 11(2):371–375
81. Rajaguru P et al (2002) Genotoxicity evaluation of polluted ground water in human peripheral blood lymphocytes using the comet assay. Mutat Res—Genet Toxicol Environ Mutagen 517(1–2):29–37
82. Rene ER, Shu L, Jegatheesan V (2019) Editorial: sustainable Eco-technologies for water and wastewater treatment. J Water Supply: Res Technol—AQUA 68(8):617–622
83. Rozendal RA, Hamelers HVM, Buisman CJN (2006) Effects of membrane cation transport on PH and microbial fuel cell performance. Environ Sci Technol 40(17):5206–5211
84. Rueter P et al (1994) Anaerobic oxidation of hydrocarbons in crude oil by new types of sulphate-reducing bacteria. Nature 372(6505):455–458
85. dos Santos AB, Cervantes FJ, van Lier JB (2007) Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology. Biores Technol 98(12):2369–2385
86. Sarma MK, Quadir MGA, Bhaduri R, Kaushik S, Goswami P (2018) Composite polymer coated magnetic nanoparticles based anode enhances dye degradation and power production in microbial fuel cells. Biosens Bioelectron 119:94–102
87. Sarmin S et al (2019) Bio-electrochemical power generation in petrochemical wastewater fed microbial fuel cell. Sci Total Environ, 695
88. Sevda S, Abu-Reesh IM (2019) Improved petroleum refinery wastewater treatment and seawater desalination performance by combining osmotic microbial fuel cell and up-flow microbial desalination cell. Environ Technol (United Kingdom) 40(7):888–895
89. Shah S, Venkatramanan V, Prasad R (2019) Microbial fuel cell: sustainable green technology for bioelectricity generation and wastewater treatment. In: Sustainable green technologies for environmental management, pp 199–218
90. Sharma M et al (2020) Bioelectrochemical remediation of phenanthrene in a microbial fuel cell using an anaerobic consortium enriched from a hydrocarbon-contaminated site. J Hazard Mater, 389
91. Sherafatmand M, Ng HY (2015) Using sediment microbial fuel cells (SMFCs) for bioremediation of polycyclic aromatic hydrocarbons (PAHs). Biores Technol 195:122–130
92. Shim H, Yang ST (2002) BTEX removal from contaminated groundwater by a co-culture of Pseudomonas putida and Pseudomonas fluorescens immobilized in a continuous fibrous-bed bioreactor. J Chem Technol Biotechnol 77(12):1308–1315
93. Singh JG, Chang-Yen I, Stoute VA, Chatergoon L (1992) Hydrocarbon levels in edible fish, crabs and mussels from the marine environment of Trinidad. Mar Pollut Bull 24(5):270–272
94. Srikanth S et al (2016) Electro-biocatalytic treatment of petroleum refinery wastewater using microbial fuel cell (MFC) in continuous mode operation. Biores Technol 221:70–77

95. Sun J et al (2011) Further treatment of decolorization liquid of azo dye coupled with increased power production using microbial fuel cell equipped with an aerobic biocathode. Water Res 45(1):283–291
96. Sun J et al (2016) Regulation of biocathode microbial fuel cell performance with respect to azo dye degradation and electricity generation via the selection of anodic inoculum. Int J Hydrog Energy 41(9):5141–5150
97. Sun J, Hu YY, Bi Z, Cao YQ (2009) Simultaneous decolorization of azo dye and bioelectricity generation using a microfiltration membrane air-cathode single-chamber microbial fuel cell. Bioresour Technol 100(13):3185–3192
98. Tacas ACJ, Tsai PW, Tayo LL, Hsueh CC, Sun SY, Chen BY (2021) Degradation and biotoxicity of azo dyes using indigenous bacteria-acclimated microbial fuel cells (MFCs). Process Biochem 102: 59–71
99. Tan SP et al (2017) Treatment of palm oil mill effluent using combination system of microbial fuel cell and anaerobic membrane bioreactor. Biores Technol 245:916–924
100. Thung WE et al (2015) A highly efficient single chambered up-flow membrane-less microbial fuel cell for treatment of azo dye acid orange 7-containing wastewater. Biores Technol 197:284–288
101. Tian X et al (2020) A comprehensive review on toxic petrochemical wastewater pretreatment and advanced treatment. J Clean Prod, 245
102. Varjani SJ, Upasani VN (2016) Carbon spectrum utilization by an indigenous strain of Pseudomonas aeruginosa NCIM 5514: production, characterization and surface active properties of biosurfactant. Biores Technol 221:510–516
103. Vasudevan N, Rajaram P (2001) Bioremediation of oil sludge-contaminated soil. Environ Int 26(5–6):409–411
104. Wang S et al (2021) Advances in research on petroleum biodegradability in soil. Environ Sci Process Impacts 23(1):9–27
105. Wang X et al (2012) Bioelectrochemical stimulation of petroleum hydrocarbon degradation in saline soil using U-tube microbial fuel cells. Biotechnol Bioeng 109(2):426–433
106. Xu H, Quan X, Xiao Z, Chen L (2017) Cathode modification with peptide nanotubes (PNTs) incorporating redox mediators for azo dyes decolorization enhancement in microbial fuel cells. Int J Hydrogen Energy 42(12):8207–8215
107. Xu H, Quan X, Chen L (2019) A novel combination of bioelectrochemical system with peroxymonosulfate oxidation for enhanced azo dye degradation and $MnFe_2O_4$ catalyst regeneration. Chemosphere 217:800–807
108. Yadav AK, Dash P, Mohanty A, Abbassi R, Mishra BK (2012) Performance assessment of innovative constructed wetland-microbial fuel cell for electricity production and dye removal. Ecol Eng 47:126–131
109. Yan Z et al (2012) Enhanced degradation of phenanthrene and pyrene in freshwater sediments by combined employment of sediment microbial fuel cell and amorphous ferric hydroxide. J Hazard Mater 199–200:217–225
110. Yan Z et al (2015) Complex interactions between the macrophyte acorus calamus and microbial fuel cells during pyrene and benzo[a]pyrene degradation in sediments. Sci Rep 5(December 2014):1–11
111. Yang Y et al (2015) Enhancing the bioremediation by harvesting electricity from the heavily contaminated sediments. Biores Technol 179:615–618
112. Yeruva DK et al (2015) Integrating sequencing batch reactor with bio-electrochemical treatment for augmenting remediation efficiency of complex petrochemical wastewater. Biores Technol 188:33–42
113. Yuan Y, Zhou S, Zhuang L (2010) A new approach to in situ sediment remediation based on air-cathode microbial fuel cells. J Soils Sediments 10(7):1427–1433
114. Zhang C, Liu G, Zhang R, Luo H (2010) Electricity production from and biodegradation of quinoline in the microbial fuel cell. J Environ Sci Health—Part A Toxic/Hazard Substan Environ Eng 45(2):250–256

115. Zhang Q et al (2012) Deciphering effects of chemical structure on azo dye decolorization/degradation characteristics: bacterial versus photocatalytic method. J Taiwan Inst Chem Eng 43(5):760–766
116. Zhang T et al (2010) Stimulating the anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. Environ Microbiol 12(4):1011–1020
117. Zhang Y et al (2015) Horizontal arrangement of anodes of microbial fuel cells enhances remediation of petroleum hydrocarbon-contaminated soil. Environ Sci Pollut Res 22(3):2335–2341
118. Zhao L et al (2019) Investigation of PAH and oil degradation along with electricity generation in soil using an enhanced plant-microbial fuel cell. J Clean Prod 221:678–683
119. Zhong D, Liu Y, Liao X, Zhong N, Xu Y (2018) Facile preparation of binder-free NiO/MnO_2-carbon felt anode to enhance electricity generation and dye wastewater degradation performances of microbial fuel cell. Int J Hydrogen Energy 43(51):23014–23026
120. Zhou L et al (2016) Microbial electricity generation and isolation of exoelectrogenic bacteria based on petroleum hydrocarbon-contaminated soil. Electroanalysis 28(7):1510–1516
121. Zsirai T et al (2018) Cleaning of ceramic membranes for produced water filtration. J Petrol Sci Eng 166:283–289

Bioremediation of Agro-Industries Pollutants Through Microbial Fuel Cells

Burcu Palas, Gülin Ersöz, and Süheyda Atalay

Abstract Valorization of the agro-industrial wastes and development of energy saving sustainable wastewater treatment systems has gained importance by the increasing demand on energy and water worldwide. Microbial fuel cell is an emerging technology with the ability of simultaneous wastewater treatment and electricity generation by harvesting the chemical energy in organic wastes and wastewaters. Agro-industry wastewaters mainly composed of carbohydrates, proteins, lipids, and various nutrients have been effectively used as a substrate for the microorganisms in bioenergy producing treatment systems. Agricultural wastes including the residues of various crops, pomace and peelings of fruits and vegetables, dairy wastes, and livestock wastes are the renewable feedstock for the microbial fuel cell systems. In addition to being used as a substrate, the agricultural wastes are used for electrode and proton exchange membrane fabrication in microbial fuel cell applications. In this chapter, a brief information and examples from the recent literature on vegetable oil processing, brewery and wine, dairy and livestock wastewater treatment, and utilization of agricultural residues in microbial fuel cells are presented. The power density, coulombic efficiency, and chemical oxygen demand removal efficiencies reported for different agricultural wastes are summarized. Finally, the challenges and future perspectives of microbial fuel cell technology are discussed.

Keywords Microbial fuel cell · Agricultural wastewater · Crop residues · Pollutant removal efficiency · Power generation

B. Palas (✉) · G. Ersöz · S. Atalay
Faculty of Engineering, Chemical Engineering Department, Ege University, İzmir 35100, Bornova, Turkey
e-mail: burcu.palas@ege.edu.tr

G. Ersöz
e-mail: gulin.ersoz@ege.edu.tr

S. Atalay
e-mail: suheyda.atalay@ege.edu.tr

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_13

1 Introduction

Wastewaters generated from domestic, industrial, agricultural, and municipal activities contain a wide variety of pollutants including toxic organic and inorganic compounds and biological components which may cause many adverse effects on environmental and human health [65]. Since many of the water resources are polluted there is a need for effective water treatment technologies [39]. In order to reach high pollution removal efficiencies an increasing capacity of equipment leading to an increase in energy consumption has been used in the wastewater treatment facilities. The electric energy consumed in the wastewater treatment processes accounts for 25–40% of the total operating costs. A significant portion of the required energy is provided from non-renewable sources. Since the use of these energy sources resulted in emission of air pollutants and environmental depletion, development of energy efficient wastewater treatment methods plays a highly important role in environmental protection [108]. Depending on the composition of the wastewater and the treatment method applied, approximately 0.5–2 kWh/m^3 of treated water energy is required for wastewater treatment. Wastewater contains nearly 3–10 times the energy (in the form of organic substance, nutritional elements, and thermal energy) required to treat it. By harvesting the chemical energy hidden in wastewater, the treatment technologies can become energy-producing processes instead of being energy-consuming applications [28]. Agricultural and food industries are one of the important contributors to worldwide environmental pollution. Effluents of agro-food industries threaten the environmental health since they contain high organic matter and traces of organic pollutants. Therefore the treatment of agro-food industry wastewaters requires appropriate and comprehensive management methods [42, 79].

2 Working Principle

Microbial fuel cell is an emerging technology producing clean and sustainable energy during the degradation of pollutants. It is a low-cost and environmentally friendly method for the treatment of biowastes, which reduces the biomass energy loss and greenhouse gas emissions. The energy in the biomass is extracted and the chemical energy in organic compounds is converted into electricity in microbial fuel cells [86, 94]. A typical microbial fuel cell (shown in Fig. 1) consists of anode and cathode chambers separated by a proton exchange membrane. Exoelectrogens, which have the ability to transfer electrons extracellularly, oxidize the organic substances into electrons and protons in the anode chamber into electrons, protons, and carbon dioxide. The diffusion of the protons through the ion exchange membrane produces a potential difference between anode and cathode. The electrons flow through the external circuit to the cathode chamber where the electrons and protons react with oxygen to form water and electrical energy is generated [84, 99].

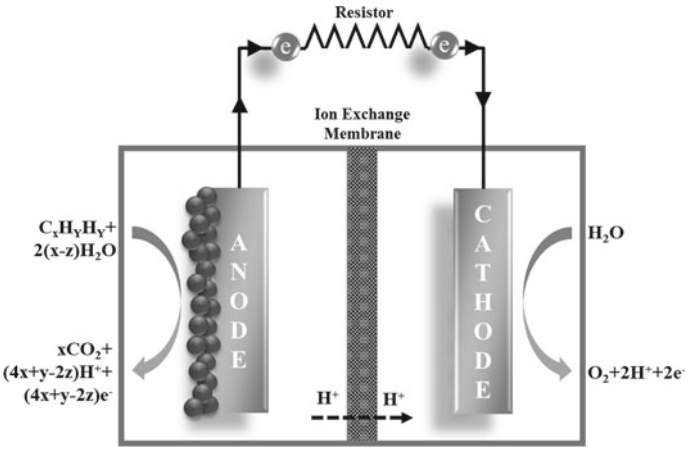

Fig. 1 Schematic representation of a typical microbial fuel cell

Many types of electrochemically active microorganisms including bacteria, archaea, and fungi have proven to be useful in microbial fuel cells. Pure or mixed culture microorganisms can be used in microbial fuel cells. The mixed cultures are synergistic communities playing different roles in the nutrient cycle. Some of the microorganisms digest nutrients while some others protect the biofilm against hazardous factors such as heavy metals. Generally, soil, marine sediments, domestic wastewater, and activated sludge including mixed cultures have been used to inoculate the microbial fuel cells. Though the growth of the pure cultures is slow, mixed cultures take longer time to reach a steady current generation in microbial fuel cells [13, 52]. The performance of microbial fuel cells depends on various factors such as reactor configuration, electrode materials, external resistance, selection of proton exchange membrane, operating pH and temperature, bacterial community, substrate, and ionic strength of electrolyte [47, 57]. Microbial fuel cells provide renewable energy to meet the global electricity requirement. This method has many advantages over other wastewater treatment methods such as [4]:

- obtaining high efficiencies due to direct conversion of organic substances into electricity,
- the ability of operation at ambient conditions,
- potential use in remote areas where the electrical infrastructure is insufficient, and,
- involving an anaerobic process reducing the bacterial biomass in comparison to the aerobic systems.

2.1 Configurations

Microbial fuel cell systems have been basically designed with dual and single chamber configurations. The primitive design for the microbial fuel cells is dual chamber or H-type configuration. Though the performance of double chambered microbial fuel cells is higher in terms of current generation and pollutant removal efficiency, the single chamber air cathode configuration is developed to reduce the cost of the process by minimizing the complexity. In the single chamber configuration there is only an anode chamber attached to the membrane cathode assembly. While one side of the cathode is bonded to the membrane, the other side is in contact with air. In addition to the basic configurations, U-tube and stack microbial fuel cell systems are available for different applications. For the large-scale operations stack microbial fuel cell configuration is used to obtain high voltage and current outputs [99, 100].

2.2 Performance Evaluation

The performance of microbial fuel cells is assessed by several measurements and calculations including the current density, power density, and coulombic efficiency. During the microbial fuel cell operations, the voltage is measured and recorded. The current, I [A], is calculated from Ohm's law:

$$I = \frac{V}{R} \tag{1}$$

where R is the external resistance [Ohm, Ω] and V is the voltage [V].

The power, P [W] is calculated by multiplying the voltage and current. The current and power are normalized to the projected surface area of the anode to determine the current and power densities [96].

$$\text{Current Density} = \frac{I}{a}\left[\frac{A}{m^2}\right];\ \text{Power Density} = \frac{P}{a}\left[\frac{W}{m^2}\right] \tag{2}$$

where a [m^2] is the surface area of the anode.

Alternatively, power can be normalized with respect to liquid volume in the anode chamber to evaluate the volumetric power density.

The coulombic efficiency is defined as the ratio of the total Coulombs calculated by integrating the current over time to the theoretical amount of Coulombs available based on the decrease in pollutant concentration. If the treatment efficiency is evaluated considering the chemical oxygen demand removal [18, 34, 95]:

$$E(\%) = \left[\frac{\int I dt}{F \times b \times v \times \frac{\Delta \mathrm{COD}}{\mathrm{MW}}} \right] \times 100 \quad (3)$$

where t is reaction time (s), F is Faraday's constant, b is the number of moles of electrons exchanged per mole of O_2, ΔCOD is the change in chemical oxygen demand (g/L), and MW is the molecular weight of the O_2, and v [L] is the volume of wastewater.

3 Treatment of Agro-Industrial Wastes and Wastewaters in Microbial Fuel Cells

The agro-food industries generate a huge amount of organic matter that can be used for energy recovery [12]. In addition to the agricultural residues in solid form, edible oil wastewaters, fruit and vegetable processing wastewaters, winery and brewery wastewaters, and the animal husbandry wastewaters including the effluents of dairy and livestock industries are categorized under the agro-food processing wastes.

3.1 Pretreatment of the Agricultural Residues

Agro-industrial wastes derived from various sources including animal husbandry, crop harvesting, edible oil production, and food and beverage processing have been found in the environment. The agricultural wastes that are used as feedstock in bioenergy production processes can be categorized into four main generations depending on their usage areas.

First generation feedstocks consist of easily available and edible food crops such as wheat, corn, rice, and sorghum. Though the food crops can be effectively used as fuel in energy production processes, the main challenge for their utilization is the food versus fuel dilemma. Second generation feedstocks include non-food crops like woody and grassy crops, residues of edible food crops (e.g., straw, husk, and bran of various crops) and bagasse, pomace, and peelings of fruits and vegetables. Third generation feedstocks comprise non-food marine biomass which is mainly algae. The fourth generation feedstocks are the engineered microorganisms which are genetically modified bacteria and algae. From first to fourth generation feedstocks are illustrated in Fig. 2 [30, 63, 74].

Agricultural residues are a promising feedstock for low-cost energy production in bioelectrochemical systems due to their renewability. However, the microorganisms in microbial fuel systems are usually unable to use lignocellulosic biomass directly for bioenergy generation. Therefore, physical, chemical, and biological pretreatment methods have been applied to make complex carbohydrate structures available for bioconversion processes [24]. In the physical pretreatment processes chipping,

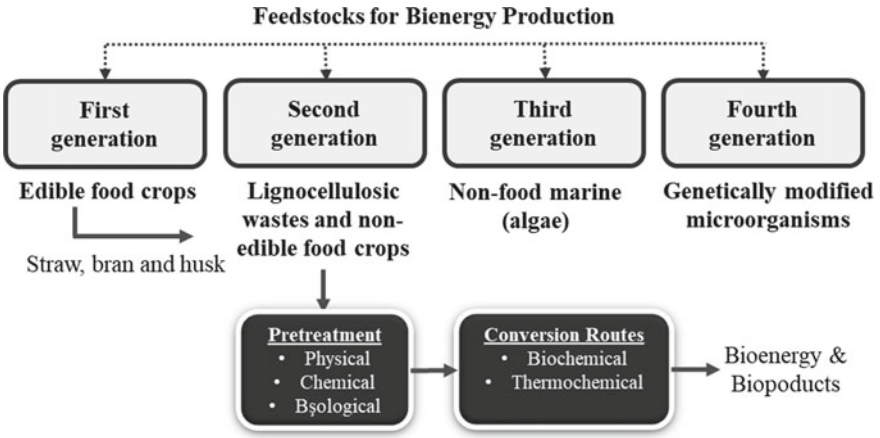

Fig. 2 Feedstocks in bioenergy production processes

milling, and grinding are applied to increase the biodegradability of agricultural biomass by reducing the size of the particles. Acidic or alkali chemicals are used in chemical pretreatment processes. Acidic pretreatment operated by using mineral or dicarboxylic acids facilitates enzymatic hydrolysis of lignocellulosic material and enhances the energy efficiency in microbial fuel cells. NaOH, KOH, hydrazine, ammonia, or lime are used as alkali pretreatment agents in case low lignin content biomass is used in microbial fuel cells. Biological pretreatment enhances the sugar yield via hydrolyzation and disruption of the crystal structure of lignocellulosic materials in the presence of bacteria and fungi [62].

3.2 Utilization of Agricultural Residues in Electrode and Proton Exchange Membrane Fabrication

A remarkable amount of agricultural residues are produced globally and it has an enormous potential to utilize biowastes [87] such as crop residues (e.g. wheat straw, corn stem, rice husk, etc.), vegetable and fruit peelings (particularly citrus peelings), fruit pomace, and sugarcane bagasse. Generally, the agro-industrial wastes have been utilized as a substrate in microbial fuel cells. Alternatively, these wastes can be used in ion exchange membrane or electrode fabrication. For instance [80], deal with the preparation of ceramic membrane by blending rice husk ash with soil. They reported that ceramic membranes having 10% rice husk ash provided higher proton mass transfer [80].

Jiao et al. [41] used rice husk-derived activated carbon in cathode fabrication and the experimental results showed that a satisfactory power density output (293.4–317.7 mW/m^2) was gained in the presence of rice husk-based electrodes [41]. Karthikeyan

et al. [43] investigated the potential of king mushroom, wild mushroom, and corn stem to be used for the fabrication of electrode materials by carbonization procedures. The maximum bio electrocatalytic current obtained by using carbon electrode derived from corn stem (3.12 mA/cm^2) was 8 times higher than the plain graphite electrode [43]. Bose et al. [11] prepared activated carbon from sugarcane waste to fabricate cathode. A power density of 0.40 mA/m^2 was obtained while 64% of chemical oxygen demand (COD) removal was achieved in the microbial fuel cell system [11]. Pepè Sciarria et al. [76] carbonized olive mill waste and salted pistachio nut shells to prepare biochar which was used as catalysts in air cathode microbial fuel cells. The maximum power density obtained by using olive mill waste-derived biochar was approximately 15 times higher than that obtained by a commercial carbon black [76].

3.3 Utilization of Agricultural Residues and Wastewaters as Substrate

Crop residues

Crop residues are one of the most suitable substrates for microbial fuel cells since they are abundantly available and can be converted into sugar monomers and protein easily in the presence of most of the microorganisms. In literature, the performance of microbial fuel cells fed by straw, stalk, and husk of various crops has been widely investigated in recent studies. Wheat straw, which contains up to 40% cellulose, 26% hemi-celluloses, and 23% lignin, is a plentifully available biomass. [72] performed the degradation of wheat straw in a dual chamber microbial fuel cell by using white rot fungi and a maximum power density of 33.19 mW was achieved [72]. Song et al. [91] utilized wheat straw in solid phase microbial fuel cell system for the removal of Pb and Zn in contaminated soil. The metal removal efficiencies of the solid phase microbial fuel cells increased with the straw ratio. By the addition of 3% wheat straw, Pb removal efficiency enhanced from 15 to 37.2%, and Zn removal efficiency increased from 7.3 to 15.1% whereas the power density increased from 10.5 to 25.7 mW m^{-2} [91]. Rice is served as the staple food for about half the world's population and its production rate reaches 731 million tons/year. Therefore, rice straw is one of the most common lignocellulosic residues that can be used in biomass-derived energy production [31]. Daud et al. [20] utilized rotten rice as an organic source for bacterial species to produce electricity and remove the metals (Cd, Pb, Cr, Ni, Co, Ag, and Cu) in wastewater. The maximum power and current densities were calculated as 2.9 mW/m^2 and 168.42 mA/m^2, respectively. The metal removal efficiencies varied between 82.2 and 99.88% [20]. Raychaudhuri and Behera [81] synthesized ceramic membranes by using soil with clay and rice husk ash. A dual chamber microbial fuel cell unit was used to treat rice husk mill wastewater. 72.4 $\pm$ 0.9 COD removal and 4.08 $\pm$ 0.08 W/m^3 of power density were obtained [81]. Cornstalk, as an abundant renewable biomass resource, can be used as a substrate in

microbial fuel cells effectively. Li et al. [50] developed a corn straw hydrolyzates-fed microbial fuel system and obtained a power density of 23.5 ± 6.0 mW/m^2 [50]. Nwaokocha et al. [67] treated Nigerian corn starch wastewater in a dual chamber microbial fuel cell. The maximum current density and power density were found to be 7.7 mW/cm^2 and 8.10 mA/cm^2, respectively [67].

Molasses residues

Molasses wastewater generated in sugar refineries contains high concentrations of organic substances including sugar, pectin, and protein. Since molasses wastewater contains large amounts of nutrient for the microorganisms, biochemical treatment methods can be applied [103]. Naina Mohamed et al. [64] treated sugar industry wastewater by using $FeMoO_4$ doped graphite plate electrode in microbial fuel cell. The power density was found to be 106 ± 3 mW/m^2. COD removal efficiency and coulombic efficiency were calculated as 79.8 ± 1.5% and 21.3 ± 0.5%, respectively [64]. Hassan et al. [32] utilized sugarcane molasses in a dual chamber microbial fuel cell and 188.5 mW/m^2 of power density was obtained. The coulombic efficiencies were in the range of 59.8–28.03% whereas the COD removal efficiency reached to 81.7% [30]. [98] realized benzene removal and power generation in a double chamber benthic microbial fuel cell fed with sugarcane waste. 82.3% of benzene removal efficiency and 24.2 mW/m^2 of power density were achieved [98].

Fruit wastes

Kondaveeti et al. [46] treated citrus waste in a single chamber air cathode microbial fuel cell for simultaneous bioelectricity generation and organic reduction. Microbial fuel cell was operated at four organic loading conditions. When the organic load increased from 3 to 12 kg/m^3, the COD removal efficiencies decreased from 45.8 to 63.8 mW/m^2, and the coulombic efficiencies decreased from 21.3 to 33.2% [46]. Moharir and Tembhurkar [61] investigated the influence of recirculation of anolyte on electricity generation using food waste substrate in a two chamber microbial fuel cell. The microbial fuel cell operation was carried out in fed-batch mode at various COD contents of 500–1250 mg/L. The recirculation improved the bioelectricity production in microbial fuel cells. The maximum current density, power density, and coulombic efficiencies were determined to be 150.30 mA/m^2, 29.23 mW/m^{2,} and 14.22% respectively, in recirculated microbial fuel cell systems [61]. Divya Priya and Pydi Setty [21] treated cashew apple juice in microbial fuel cell for bioelectricity production. The maximum power density was calculated as 31.57 mW/m^2 at a current density of 350 mA/m^2 [21]. He et al. [33] used an air cathode single chamber microbial fuel cell to treat fruit waste extracts and sludge fermentation liquid. Four microbial fuel systems which were fed by glucose, fruit waste extracts (FWEs), sludge fermentation liquid (SFL), and mixture of SFL and FWEs were operated. The electricity generation was improved significantly by adding fruit waste extracts. The soluble organic matter removal was above 90% in all of the microbial fuel cell (MFC) systems. The bioelectricity conversion efficiencies for SFL-MFC, FWEs-MFC, and the mixture-MFC were evaluated as 1.061, 0.718, and 1.391 kWh/kg COD, respectively [33]. Kebaili et al. [44] utilized the fruit wastes to prepare fermented fruit

juice inoculum. They used a two chambered microbial fuel cell consisting of platinum grid cathode and graphite rod anode inoculated with fruit leachate. Sucrose and fructose were used as fuel and the performances of graphite carbon and graphite felt bio-anodes were compared. The power dentistry reached up to 20 mW/m^2 in the presence of graphite carbon whereas graphite felt provided a power density of 25 mW/m^2 [44].

Solid phase applications

In addition to the liquid phase applications, fruit wastes can be utilized in solid phase microbial fuel cells. Hariti et al. [29] studied on the reduction of agro-industrial waste pollutants and energy production in a solid phase microbial fuel cell by utilization of the citrus industry wastes as substrate. The marine sediments were mixed with orange peel waste and treated in microbial fuel cells. The effect of the orange peel amount and external resistance on bioelectricity generation and organic matter reduction were investigated. The maximum power density and total organic carbon were recorded as 0.28 W/m^2 and 55%, respectively [29]. The recent studies on microbial fuel cell performances using agricultural wastes and wastewater as a substrate is reported in Table 1.

Edible oil wastewaters

Olive, palm, coconut, cottonseed, peanut, rapeseed, soybean, and sunflower seed are the major sources used for vegetable oil production in the world. The edible oil industries generate large amounts of wastewater and the organic and nutrient constituents of the untreated wastewaters damage the aquatic life. Recently, instead of applying ordinary treatment methods, conversion of the agricultural wastes into useful products or energy has gained attraction due to the fast growth of vegetable oil industries [49]. For instance, [26] investigated the performance of the mirobial fuel cell by using vegetable oil industry wastewaters as a substate. The power densities at 25 and 35 °C were found to be 2166–6119 mW/m^2, respectively. The coulombic efficiencies and the COD removal efficiencies varied between 33.0–36.5% and 80%–90%, respectively [26]. Liu and Vipulanandan [53] used metallic nanoparticles of Fe, Ni, and Fe/Ni were used as cathode catalysts to improve power production in a dual chamber microbial fuel cell fed with used vegetable oil. Fe nanoparticles promoted bacterial growth and biosurfactant formation and showed the greatest catalytic effect on the microbial fuel cell performance by incresing the power density up to 66.4 mW/m^3 [53].

Olive oil and palm oil processing effluents discharged from the vegetable oil industries are the most commonly treated wastewaters in microbial fuel cells.

Olive oil wastewaters

Olive oil production process is one of the most significant commercial agro-food industries in Mediterranean countries due to the growing interest in olive oil consumption [58]. In literature it reported that approximately 8×10^6 tons of olive mill wastewater is generated worldwide annually and nearly half of the total volume of

Table 1 Performances of microbial fuel cells fed with various agricultural wastes and wastewaters

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Daud et al. [20]	Rotten rice	Single chamber	Graphite rods	Graphite rods	Pond wastewater	PD: 2.9 mW/m^2	82.2–99.88% metal removal
Pal and Sharma Raychaudhuri and Behera [72]	Wheat straw	Dual chamber	Carbon fiber	Stainless steel	In cathodic chamber: white rot fungi in anodic chamber: exoelectrogenic yeast	PD: 12.9–33.19 mW/m^2	
Umar et al. [81]	Rice mill wastewater	Dual chamber	Stainless steel mesh	Graphite plate	Anaerobic sludge collected from the bottom of a pond	PD: 4.08 ± 0.08 W/m^3	72.4 ± 0.9% COD removal
[98]	Sugarcane waste	Dual chamber benthic MFC	Cylindrical graphite rods	Cylindrical graphite rods		PD: 24.2 mW/m^2	82.3% benzene bioremediation
Naina Mohamed et al. [64]	Sugar industry wastewater	Dual chamber	$FeMoO_4$ doped graphite plate	Plain graphite plate		PD: 106 ± 3 mW/m^2 CE: 21.3 ± 0.5%	79.8 ± 1.5% COD removal
Li et al. [50]	Corn straw hydrolyzates	Dual chamber	Carbon cloth	Carbon cloth	*K. pneumoniae S. oneidensis*	PD: 23.5 ± 6.0 mW/m^2	
Nwaokocha et al. [67]	Corn starch wastewater	Dual chamber	Iron electrode	Iron electrode	Wastewater from corn processing plant	PD: 7.7 mW/cm^2	

(continued)

Table 1 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
He et al. [33]	Fruit waste extracts (FWEs), Sludge fermentation liquid, (SFL) Mixture of SFL&FWEs	Single chamber	Carbon brush	Plain carbon cloth and covered with a platinum catalyst	Anaerobic bioreactor used for wastewater treatment	PD: 0.123–0.197 W/m^2	90% soluble organic matter removal
Kondaveeti et al.[46]	Citrus peel extract	Single chamber	Plain graphite plate	Plain graphite plate	Effluent of anaerobic digestive reactor operated with food waste leachate	PD: 48.5–71.1 mW/m^2 CE: 21.3 33.2%	45.8–63.8% COD removal
Moharir and Tembhurkar [61]	Food waste leachate	Dual chamber	Carbon rod	Carbon rod	The mixture of food industry sludge and cow dung slurry	PD: 29.23 mW/m^2, CE: 14.22–29.32%	58.97–72.27% COD removal
Hariti et al. [29]	Orange peel wastes mixed with marine sediments	Single solid phase microbial fuel cell	Graphite rod	Graphite rod	Dewatered sludge from anaerobic digester	PD: 242.7–282.28 mW/m^2	22%-55% TOC removal

PD: Power Density, CE: Coulombic efficiency, MFC: Microbial fuel cell

the olive oil mill output is released as wastewater [7]. The olive oil wastewater generated per unit mass of olive processed values is reported as 40–55 L/100 kg of olives for traditional batch press and 80–120 L/100 kg of olives for continuous solid–liquid centrifuge systems. The chemical and biochemical oxygen demand of the olive oil wastewaters generally varied between 80–200 g/L and 50–100 g/L, respectively [25]. One m^3 of olive oil mill wastewater is equivalent to 100–200 m^3 of domestic sewage in terms of pollution influence. Olive oil mill wastewaters contain high amounts of sugars, proteins, phenols, lipids, and phosphorus that microorganisms can metabolize [1, 97]. The release of improperly treated olive oil wastewaters may result in contamination of soil and water resources, phytotoxic impacts on aquatic fauna, and ecological equilibria. The conventional wastewater treatment methods usually do not provide a high effectiveness for the elimination of the hazardous pollutants in the olive oil mill wastewaters [69]. Microbial fuel cell treatment is a promising solution for the removal of pollutants in olive oil wastewaters. [8] investigated the treatment of phenol containing synthetic wastewater and olive oil wastewater in dual chamber microbial fuel cells in the presence of phenol-adapted activated sludge and Ralstonia eutropha. In case the olive oil wastewater was fed to the microbial fuel cell the highest power density was found to be a value of 7.8 mW/m^2 whereas the COD removal efficiency was 48% [8]. Pepè Sciarria et al. [78] treated the mixtures of olive oil wastewater and domestic wastewater in a single chamber microbial fuel cell. A power density of 124.6 mW/m^2 was achieved. The total chemical oxygen demand (TCOD) and BOD_5 removal efficiencies were calculated as 60% and 69%, respectively, yielding 29% of coulombic efficiency [78].

Palm oil wastewaters

Palm oil is an inexpensive product which has many application areas in food, cosmetic, pharmaceutical, and biofuel industries [14]. Palm oil wastewaters contain high organic content mainly composed of oil and fatty acids, carbohydrates, proteins, and a remarkable amount of cellulose, which make the palm oil wastewaters suitable for biological treatment processes. Usually, generation of one ton of crude palm oil requires approximately 5–7.5 tons of water, and nearly half of the used water produces palm oil mill effluent [2]. High chemical and biochemical oxygen demand content and organic nitrogen and phosphorus concentration level of the palm oil wastewaters can cause significant environmental problems if discharged without an efficient treatment [15]. Sarmin et al. [82] used palm oil mill effluent as a substrate in a two chambered microbial fuel cell. The power density was improved up to 500 mW/m^2 in the presence of yeast-bacteria inoculum whereas the chemical oxygen demand removal efficiency was enhanced up to 90% [82]. Islam et al. [37] investigated the performance of a dual chamber microbial fuel cell inoculated with *Klebsiella varicola* for the treatment of palm oil mill effluent. 4.5 W/m^3 power density and 63% coulombic efficiency were evaluated while the chemical oxygen demand removal efficiency was 58% [37]. Sedighi et al. [83] treated palm oil wastewater in a two chambered microbial fuel cell. The highest power density at the optimum conditions was 58.19 mW/m^2 and the maximum COD removal was calculated as 94.8% [83]. Baranitharan et al. [9] operated a double chamber microbial fuel cell using diluted

palm oil mill effluent. The maximum power density, COD removal efficiency, and coulombic efficiency were evaluated as 22 mW/m^2, 70%, and 24%, respectively [9]. A list of microbial fuel cell performances using vegetable oil wastes as a substrate is reported in Table 2.

3.4 Winery and Brewery Wastewaters

Winery wastewaters

Winery wastewater is mainly generated from the washing steps operated to clean tanks, floors, equipment, and barrels in the wine production processes. Additionally, product losses, bottling facilities, and filtration units contribute the winery wastewater generation. Winery effluents contain many pollutants including ethanol, sugars, organic acids, and phenolic compounds. The estimated winery residues are between 1.3 and 1.5 kg per liter of wine produced, 75% of which is winery wastewater. It is reported that the chemical oxygen demand concentration of winery wastewaters are in the range of 500–45,000 mg/L and total suspended solids varied between 12 and 7300 mg/L whereas the biological oxygen demand concentration is approximately 0.4–0.9 of the chemical oxygen demand value [36, 85]. The excessive use of water, pesticide use, and presence of semi-solid organic wastes including grape marc, vinasses, lees, and sludge, and the seasonal changes in the wastewater parameters make the winery wastes difficult to be treated [10].

Therefore, conventional treatment methods are generally not sufficient for the removal of the wastes generated by wineries. Microbial fuel cell is a promising solution for the treatment of winery wastewaters. Liu et al. [54] operated an air cathode microbial fuel cell inoculated with anaerobic winery sludge to treat synthetic winery wastewater The maximum power density and the COD removal efficiency were found to be 54 mW/m^2 and 77 $\pm$ 7%, respectively [54]. Penteado et al. [75] investigated the winery wastewater treatment in the presence of various carbon electrodes in a dual chamber microbial fuel cell. The highest power density was found at 420 mW/m^2 by using carbon felt and the maximum COD removal was around 11% [75]. Pepe Sciarria et al. [77] studied on the treatment of white and red wine lees in a single chamber air cathode microbial fuel cell. They reported that the power densities were calculated as 111 and 262 mW/m^2 by using red and white wine lees, respectively. The reduction of chemical and biochemical oxygen demand was 27% and 83%, respectively for red wine lees while the removal efficiencies were evaluated as 90% and 95% for white wine lees [77].

Brewery wastewaters

Brewery is one of the sectors that consumes a large amount of water and energy. During the beer production extracts of hops, malt, sugar, and water are mixed and fermented by using yeast. Beer is reported as the fifth most consumed beverage in the world. The discharged by-products such as spent grains, and yeast surplus

Table 2 Performances of microbial fuel cells fed with vegetable oil wastewaters

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Bagheri et al. [8]	Olive oil wastewater	Dual chamber	Graphite electrode plates	Graphite electrode plates	Phenol-acclimated activated sludge and *Ralstonia eutropha*	PD: 7.8 mW/m^2	48% COD removal
Firdous et al. [26]	Vegetable oil industrial effluents	Dual chamber	Titanium rod	Carbon cloth	Sewage sludge	PD: 2166–6119 mW/m^2 CE: 33.0–36.5%	80–90% COD removal
Sedighi et al. [83]	Palm oil mill effluent	Dual chamber	Plain carbon paper	Carbon paper Coated with Pt	Anaerobic sludge, consisting of palm oil mill effluent	PD: 58.19 mW/m^2	94.8% COD removal
Liu and Vipulanandan [53]	Used vegetable oil	Dual chamber	Carbon fiber brushes	Fe, Ni, or Fe/Ni coated carbon brushes	Bacteria *Serratia sp*	PD: 26.0–66.4 mW/m^3	
Sarmin et al. (2020)	Palm oil mill effluent	Dual chamber	Polyacrylonitrile carbon felt	Polyacrylonitrile carbon felt	Combination of *Saccharomyces cerevisiae*, *Klebsiella variicola,* and *Pseudomonas aeruginosa*	PD: 500 mW/m^2	90% COD removal
Islam et al. [37]	Palm oil mill effluent	Dual chamber	Carbon brush	Carbon brush	*Klebsiella variicola*	PD: 4.5 W/m^3 CE: 63%	58% COD removal
Baranitharan et al. [9]	Palm oil mill effluent	Dual chamber	Polyacrylonitrile carbon felt	Polyacrylonitrile carbon felt	Anaerobic sludge	PD: 22 mW/m^2 CE: 24%	70% of COD efficiency

(continued)

Table 2 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Pepè Sciarria et al. [78]	Olive oil mill wastewater and domestic wastewater	Single chamber	Brush anodes made of a core of two titanium wires with graphite fibers	Platinum catalyst on carbon cloth	Domestic wastewater	PD: 124.6 mW/m^2 CE: 29%	60% of TCOD and 69% BOD5 removal efficiencies

PD: Power Density, CE: Coulombic efficiency, MFC: Microbial fuel cell

are responsible for environmental pollution. Additionally, cleaning of tanks, bottles, equipment, and floors generates large amounts of wastewater. In order to produce 1 L of beer, 3–10 L of wastewater is generated depending on the production process [6, 89]. Brewery wastewaters are generally more concentrated in comparison to domestic wastewater by tenfold varying from 3000 to 5000 mg COD/L. Brewery wastewater can be utilized as substrate effectively in microbial fuel cells due to the low strength and low inhibitory compound concentration and high carbohydrate content of the food-based wastewater [24, 28]. Negassa et al. [66] studied on brewery industry wastewater treatment in a double chambered microbial fuel cell inoculated with locally isolated microorganisms. The chemical oxygen demand, biochemical oxygen demand, and total suspended solid removal efficiencies were found to be in the range of 79 − 83%, 55–67%, and 76–78%, respectively, while 0.8 W/m^3 of power density was achieved [66]. Lu et al. [55] investigated the brewery wastewater treatment performance of a twenty-liter continuous flow microbial fuel cell. It is depicted that the maximum power density, coulombic efficiency, and chemical oxygen demand removal efficiencies were 1.61 mW/m^2, 13.9%, and 94.6%, respectively [55].

Stackable configurations

Yuvraj and Aranganathan [106] analyzed the stacked microbial fuel cell performances. Series–parallel setup conjugation yielded a maximum power density of 1345 mW/m^2 and 81% of chemical oxygen demand removal by using brewery effluent [106]. Dong et al. [22] designed a ninety liter stackable microbial fuel cell system and used for brewery wastewater treatment. Diluted wastewater and raw wastewater were used at the first and second stages, respectively. The chemical oxygen demand and suspended solid removal efficiencies were 84.7% and 81.7% at the first stage and 87.6% and 86.3% at the second stage, respectively. The power densities changed from 138 ± 4 to 181 ± 21 mW/m^2 [22]. The performances of microbial fuel cells fed with winery and brewery wastewaters are shown in Table 3.

3.5 Dairy Industry Wastewaters

The dairy industries manufacture various products including pasteurized milk, skim milk, cream, butter, cheese, yoghurt, ice cream, and milk dessert via transformation of raw milk. The dairy wastewaters containing carbohydrates, lipids, proteins, phosphorous, and nitrates are characterized by high concentrations of chemical and biochemical oxygen demand, oil and grease, total suspended solids, total nitrogen, and total phosphorus [45, 88, 102]. Dairy industry is one of the noticeable sectors, which generates waste thrice the volume of milk produced, and also it discharges a large amount of processed water varying between 3.739 and 11.217 mm^3 of waste annually. The manufacturing steps of dairy products involve water consuming units such as tanks, cleaning stores, exchangers, channels, and homogenizers generating effluents with a high organic waste content [40]. The composition of dairy wastewater varies depending on the product type, milk constituents including lactose, casein, and

Table 3 Performances of microbial fuel cells fed with winery and brewery wastewaters

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Liu et al. [54]	Synthetic winery wastewater	Air cathode MFC	carbon fiber mesh	Carbon cloth coated with Nafion and polytetrafluoroethylene on different sides	Anaerobic winery sludge	PD: 54 mW/m^2	77 ± 7% COD removal
Penteado et al. [75]	Winery wastewater	Dual chamber	Carbon felt carbon cloth and carbon paper	Carbon felt carbon cloth and carbon paper	Activated sludge reactor	PD: 420 mW/m^2 (by using carbon felt)	11% COD removal (by using carbon felt)
Pepe Sciarria et al. [77]	White and red wine lees	Single chamber	Brush anodes made of a core of two titanium wires with graphite fibers	Platinum catalyst on carbon cloth	Effluent Coming from other MFCs inoculated with denitrification tank wastewater	PD: 262 mW/m^2 for white lees, 111 mW/m^2 red wine lees	90% TCOD and 95% BOD_5 removal for white wine lees, 27% TCOD and 83% BOD_5 removal for red wine lees
Negassa et al. [66]	Brewery wastewater	Dual chamber	Graphite rod	Graphite rod	Locally isolated microorganisms from brewery waste sludge	PD: 0.8 W/m^3	79 − 83% COD removal, 55–67% of BOD removal, 76–78% TDS removal
Lu et al. [55]	Brewery wastewater	Dual chamber	Carbon cloth	Carbon cloth	Lagoon sediment and diluted brewery wastewater	PD: 1.61 mW/m^2 CE:5.5–13.9%	75.3–94.6% COD removal
Yuvraj and Aranganathan [106]	Brewery wastewater	Stacked dual chamber with salt bridge	Graphite blocks	Graphite blocks	*Klebsiella pneumonia* isolated from sewage water	PD: 1345 mW/m^2	81% COD removal

(continued)

Table 3 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Dong et al. [22]	Brewery wastewater	Stackable baffled microbial fuel cell	Carbon brushes	Rolling cathodes made of activated carbon and polytetrafluoroethylene	Brewery wastewater	PD: 138 ± 4–181 ± 21 mW/m^2	84.7–87.6% COD removal 81.7–86.3% TSS removal

PD: Power Density, CE: Coulombic efficiency, MFC: Microbial fuel cell

inorganic salts, unit operations in the process, and the detergents and disinfectants used for washing. The chemical oxygen demand and biochemical oxygen demand changed between 80–95,000 mg L^{-1} and 40–48,000 mg L^{-1}, respectively [3].

Treatment in dual chamber MFC

Sivakumar [90] treated dairy industry wastewater in a double chambered salt bridge microbial fuel cell. The maximum chemical oxygen demand removal efficiency reached to 89.7%. The current and power densities obtained from dairy industry wastewater treatment were 1309.09 mA/m^2 and 1067.33 mW/m^2, respectively [90].

Cecconet et al. [12] operated two parallel microbial fuel cell reactors continuously for the treatment of real dairy industry wastewater. The results showed that high organic matter removal can be accomplished by recovering a maximum power density of 27 W/m^3. The average COD removal efficiencies were 80 ± 10% for the first microbial fuel cell reactor and 83 ± 11% for the second reactor. On average, the first microbial fuel cell reactor exhibited a coulombic efficiency of 20 ± 16%, while the second reactor provided a lower efficiency of 14 ± 11% [12].

Treatment in single chamber MFC

Choudhury et al. [16] treated real dairy wastewater in a single chamber microbial fuel cell inoculated with *Shewanella algae*. The maximum power and current densities reached to 50 mW/m^2 and 141 mA/m^2, respectively. The coulombic efficiency was calculated as 27.45% whereas 92.21% of COD removal efficiency was obtained [16]. Marassi et al. [59] investigated the dairy wastewater treatment and energy generation performance of an air cathode microbial fuel cell. The scaled-up approach revealed that a maximum power density of 0.48 W/m^3 was accomplished. Total chemical oxygen demand and total biochemical oxygen demand removal efficiencies were determined as 93% and 95%, respectively [59]. Choudhury et al. [17] investigated the power generation from simulated and real dairy wastewater treatment in a single chamber microbial fuel cell by using Escherichia coli −K-12. After the two consecutive synthetic dairy wastewater feedings, real dairy wastewater feedings at various chemical oxygen demand values were carried out. The power density and the current density were found to be 1.05 W/m^2 and 8.01 A/m^2 respectively. 67.53% of coulombic efficiency and 95.45% of COD removal efficiency were achieved [17]. Vilas Boas et al. [101] operated microbial fuel cell inoculated with *Lactobacillus pentosus* to treat dairy industry effluents. A maximum power density of 5.04 ± 0.39 mW/m^2 was accomplished whereas the COD removal efficiencies were in the range of 42–58% [101].

Treatment of cheese whey

Antonopoulou et al. [5] studied on valorization of cheese whey in a single chamber air cathode microbial fuel cell. Microbial fuel cell was fed with two different substrates which are filter-sterilized raw cheese whey and pretreated-acidified diluted cheese whey to investigate the influence of the organic load. According to the experimental

results, filter-sterilized cheese whey was a promising substrate for electricity production. When filter-sterilized wastewater was replaced by acidified-pretreated wastewater, the performance of the microbial fuel cell was not affected significantly [5]. Ghasemi et al. [27] applied two different biological methods for the treatment of cheese whey and concentrated cheese whey. In the first method, fermentation of cheese whey were performed in an immobilized cell reactor to produce lactic acid. In the second method whey and concentrated cheese whey were utilized as carbon sources in a microbial fuel cell. The power densities were found to be 188.8 and 288.12 mW/m^2 for whey and concentrated whey-fed microbial fuel cells while the COD removal efficiencies were evaluated as 95% and 86% respectively [27].

Treatment of mixtures

The performance of the microbial fuel cell systems was tested for the treatment of dairy wastewater containing various types of mixtures. For instance [60], studied on biofuel and bioenergy production from the mixture of cheese whey and livestock waste. Biogas production and electricity generation were achieved in an anaerobic co-digestion reactor and a dual chambered microbial fuel cell, respectively [60]. Tajdid Khajeh et al. [93] realized the treatment of mixed dairy and dye wastewaters. Various dairy products comprising milk, cheese water, and yogurt water were mixed with Acid Orange 7 dye in different combinations and fed to the microbial fuel cell as substrate. The maximum power density, coulombic efficiency, and decolorization were obtained as 44.05 mW/m^2, 1.76%, and 92.18% respectively, for the mixture of cheese water and Acid Orange 7 [93]. Colombo et al. [19] used four sets of membraneless single chamber microbial fuel cells fed with different agricultural organic substrates in the form of dried powder. Cheese whey, kitchen waste (a mixture of animal and vegetal food), fish waste, and citrus pulp were utilized as substrate in microbial fuel cells. The maximum COD removal was evaluated as 98.77% in the presence of obtained cheese whey substrate and the maximum coulombic efficiency was calculated as 9.91% in the presence of kitchen waste [19]. A list of microbial fuel cell performances using dairy wastewater as substrate is presented in Table 4.

3.6 Livestock Wastewaters

A remarkable increase in demand for animal products has been observed worldwide and the livestock industry has been developed fast in the last decades to produce the required amount of meat, eggs, and milk. More concentrated and large-scale livestock farms have been established to enhance the production capacity, which increased the livestock wastewater generation in turn. Livestock wastewaters are composed of manure, urine, and flushing water and contain nutrients, heavy metals, antibiotics, and pathogens [35, 107].

Livestock wastewaters are generally characterized by high chemical oxygen demand, biological oxygen demand, nitrogen, and phosphorus content. High concentrations of phosphorus and nitrogen in livestock effluents contribute to results in

Table 4 Performances of microbial fuel cells fed with dairy wastewaters

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Antonopoulou et al.[5]	Cheese whey wastewater	Single-chamber four air–cathode MFC	Graphite granules	Plexiglas tubes covered by GORE-TEX® cloth coated with MnO_2	Cheese whey (without extra microbial source)	PD: 1.57 W/m^3 CE: 4.4%	63.6% COD removal
Choudhury et al.[16]	Real dairy wastewater	Single chamber	Carbon-coated carbon cloth	Pt/C	*Shewanella algae*	PD: 50 mW/m^2 CE: 27.45%	92.21% COD removal
Choudhury et al. [17]	Simulated and real dairy wastewater	Single chamber	Carbon-coated carbon cloth	Pt/C	*Escherichia coli -K-12*	PD: 1.05 W/m^2 CE: 67.53%	95.45% COD removal
Marassi et al. [59]	Raw dairy wastewater	Single chamber	Multi-electrode consisted of carbon cloth attached to reticulated vitreous carbon foam and graphite cylinders	Pt loaded carbon cloth	Electrogenic bacterial consortium of Shewanella oneidensis and clostridium butyricum	PD: 0.48 W/m^3	Removal of 93% COD 95% BOD 100% nitrate 57% organic nitrogen 90% sulfate 90% organic phosphorus
Sivakumar [90]	Dairy wastewater	Double chambered salt bridge microbial fuel cell	Ferrite circular electrode	Ferrite circular electrode	Sludge obtained from primary clarifier of a dairy industry wastewater treatment plant	PD. 1067.33 mW/m^2	89.7% COD removal

(continued)

Table 4 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Cecconet et al. [12]	Dairy wastewater	Two parallel dual chamber MFC reactors	Graphite rod	Graphite rod	30% aerobic activated sludge, 10% dairy waste water, 60% distilled water	PD: 27 W/m^3 CE: 20 ± 16% for the first MFC and 14 ± 11% for the second MFC	COD removal of 80 ± 10% for the first MFC reactor 83 ± 11% for the second MFC reactor
Tajdid Khajeh et al. [93]	– Yogurt water + Acid Orange 7 – Milk + Acid Orange 7 – Cheese water + Acid Orange 7	Dual chamber	Graphite plates	Graphite plates	Anaerobic activated sludge from wastewater treatment plant	PD: 44.05 mW/m^2 CE: 0.21–1.76%	56.66–84.56% COD removal 77.13–92.18% decolorization
Colombo et al. [19]	– Cheese whey – Kitchen waste – Fish waste – Citrus pulp	Single chamber	Rolled carbon cloth sheet	Carbon cloth sheets modified by gas diffusion layer	Anaerobic sludge of a biogas production plant	CE: 2 -10%	61.4–98.77% COD removal
Michalopoulos al. [60]	Cheese whey and manure of pig, cow, poultry, and sheep	Dual chamber	Carbon fiber paper	Carbon cloth coated with a Pt catalyst	Anaerobic sludge	PD: 50 mW/m^2 CE: 2.1%	67–75% COD removal
Ghasemi et al. [27]	Cheese whey and concentrated cheese whey	Dual chamber	Plain carbon paper	Carbon paper coated with Pt	Anaerobic sludge from palm oil mill effluent	PD: 188.8–288.12 mW/m^2	86–95% of COD removal
Vilas Boas et al. [101]	Dairy wastewater	Single chamber	Carbon fiber graphite brush	Plain carbon cloth coated with platinum black	*Lactobacillus pentosus*	PD: 5.04 ± 0.39 mW/m^2	42–58% COD removal

eutrophication of receiving water bodies [71]. Therefore, the application of efficient treatment methods is needed for the removal of contaminants in livestock wastewaters.

Cow manure and urine

Syed et al. [92] operated a single chamber microbial fuel cell that was fed with pretreated cow dung (PCD) and pretreated buffalo dung (PBD). The highest chemical and biochemical oxygen demand removal efficiencies and the power density were evaluated as 80%, 87%, and 12.75 mW/m^2, respectively, with PBD. The coulombic efficiencies obtained with PBD and PCD were calculated as 0.53% and 0.48%, respectively [92]. Xin et al. [105] used Cu_2O decorated reduced graphene oxide composite as cathode catalyst for the treatment of cattle wastewater. The maximum power density and coulombic efficiency of 3D air cathode microbial fuel system reached to 1362 mW/m^2 and 54.9%, respectively, and the average COD removal rate was found to be 71.5% [105]. Xie et al. [104] treated cow manure slurry by using a single chamber air-cathode microbial fuel cell. The performances of microbial fuel cells inoculated with activated sludge or domestic sewage were compared to the performance obtained with raw cow manure slurry. The maximum power density and chemical oxygen demand removal were found to be 1.259 ± 0.015 W/m^2 and 84.72 ± 0.48%, respectively, by using activated sludge and cow manure sludge [104].

Jadhav et al. [38] treated cow's urine in a dual cell microbial fuel cell. The power density varied between 3.08 and 5.23 W/m^3 and the highest chemical oxygen demand, nitrate, and carbohydrate removal efficiencies were 79%, 77 ± 4.1%, and 80 ± 3.9%, respectively [38].

Swine wastewater

Li et al. [51] used an airlift-type photosynthetic microbial fuel cell for the treatment of swine wastewater. Swine wastewater was used as inoculum in anodic chamber whereas algae was used in cathodic chamber. The maximum value of power density was 3.66 W/m^3 and the removal efficiencies of chemical oxygen demand, total organic carbon, NH_4^+–N, and total phosphorous were calculated as 96.3%, 95.1%, 99.1%, and 98.9%, respectively [51]. Lai et al. [48] treated swine wastewater collected from animal husbandry. Various 3D laminated composite electrodes were prepared by using zinc-coated metallic wires or stainless steel wires as sheath and carbon fibers as core. The maximum power density, coulombic efficiency, and the chemical oxygen demand removal efficiencies were between 0.6–121.9 mW/m^2, 0.6–45.8% and 30.4–81.5%, respectively, depending on the electrode type [48]. Ma et al. [56] investigated the effect of hydraulic retention time on microbial fuel cell performance in treatment of pig manure and a swine wastewater mixture. The power densities, chemical oxygen demand, and coulomb efficiency were in the range of 0.5–13 mW/m^2, 59–83%, and 0.2–7.1%, respectively, depending on the hydraulic retention time varying between 13 and 20 days [56]. The recent studies on treatment of livestock wastes in microbial fuel cell are summarized in Table 5.

Table 5 List of livestock wastewaters that are used in microbial fuel cells and their performances

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Li et al. [51]	Swine wastewater	Airlift-type photosynthetic MFC (dual chamber)	Carbon brush	Carbon fiber cloth containing Pt catalyst	In anodic chamber: Swine wastewater in cathodic chamber: *C. vulgaris*	PD:3.66 W/m^3	Removal of 96.3% COD, 95.1% TOC, 99.1% NH_4^+-N, 98.9% total phosphorous
Xin et al. [105]	Cattle wastewater	Single-chamber	Carbon fiber brush	Carbon cloth (PTFE coated on air-facing side, Pt/C or Cu_2O/rGO coated on the water-facing side)	Dairy manure from dairy farm	PD: 1166–1362 mW/m^2 CE: 53.5–54.9%	69.8%-71.5%, COD removal
Syad et al. [92]	Cattle manures (cow dung and buffalo dung)	Membraneless MFC	Square carbon paper	Pt-coated carbon paper		PD: 5.55–12.75 mW/m^2 CE: 0.48–0.53%	72–80% of COD removal 81–87% of BOD removal

(continued)

Table 5 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Lai et al. [48]	Double chamber	Swine wastewater	Carbon fibers combined with zinc-coated metallic wires or stainless steel wires	Carbon fibers combined with zinc-coated metallic wires or stainless steel wires	Swine wastewater	PD: 0.6–121.9 mW/m^2 CE: 0.6–45.8%	30.4–81.5% COD removal
Xie et al. [104]	Cattle manure slurry (CMS)	Single chamber	Anode brushes made of graphite fibers around a titanium core	Activated carbon and PTFE	Activated sludge (AS) or domestic sewage (DS)	PD: 0.901 ± 0.005–1.259 ± 0.015 W/m^2 (using AS + CMS) CE: 40.39 ± 0.7% - 69.15 ± 0.39	67.06 ± 0.52% - 84.72 ± 0.48% COD removal
Jadhav et al. [38]	Cow's urine	Dual chamber	Carbon felt	Carbon felt	Mixed anaerobic sludge collected from septic tank bottom	PD: 3.08–5.23 W/m^3	Removal of 79% COD 77 ± 4.1% nitrate 80 ± 3.9% carbohydrate

(continued)

Table 5 (continued)

References	Feed source	MFC type	Anode	Cathode	Inoculum	Electricity generation	Removal efficiency
Ma et al. [56]	Up-flow two-chamber MFC	Mixture of real pig manure and swine wastewater	Carbon cloth	Carbon cloth		PD: 0.5–13 mW/m^2 CE: 0.2–7.1%	59–83% COD removal

PD: Power Density, CE: Coulombic efficiency, MFC: Microbial fuel cell

4 Conclusion and Future Perspective

Microbial fuel cell technology as an alternative sustainable wastewater treatment method has a great potential for energy generation and utilization of agro-industrial wastes and wastewaters. The chemical energy in the agricultural wastes is converted into electricity in microbial fuel cells. However, there are still some bottlenecks associated to the application of microbial fuel cells. The main challenges are the insufficient power output and the difficulty in scale up limiting the industrial applications. The direct movement of electrons from the microorganism to the electrode is limited by the transfer resistances which are denoted as overpotentials. The overpotentials reduce the potential obtained from the microbial fuel cell and decline the energy efficiency. The losses can be categorized as (i) the activation overpotentials occurring due to the activation energy that has to be overcome by the reacting species, (ii) concentration polarization expressed as the inability to maintain the initial substrate concentration in the bulk medium at high power densities, and (iii) ohmic losses arising from the electrode, membrane and electrolyte resistances [23, 70]. Considering the energy losses in microbial fuel cell systems, development of innovative low-cost electrodes providing high electrical conductivity, favoring biofilm formation, and improving the stability is one of the significant issues this technology should focus on in the future. Additionally, fabricating ecofriendly membrane materials with enhanced proton conductivity, less crossover of substrate and O_2, and anti-fouling features is needed for efficient microbial fuel cell operations [68, 73]. Various approaches have been used in recent researches to fabricate environmentally friendly and efficient electrode and proton exchange membranes. Utilization of agricultural wastes particularly in the form of carbonized materials contributes not only the valorization of wastes but also the development of sustainable electrode and membrane materials with high surface areas. Using biocathodes consisting of microorganisms is an alternative solution to improving the power output of the microbial fuel systems. Even though very high pollutant removal efficiencies exceeding 90% can be achieved in agro-industrial wastewater treatment, reaching high coulombic efficiencies affected by the energy losses is a challenge for microbial fuel cell systems. Consumption of substrate in undesired reactions such as the direct oxidation of substrate by diffused oxygen and the metabolic reactions of non-exoelectrogens species are the important factors causing energy losses. Selection of appropriate microorganisms, electrodes, and membranes and operation at optimum reaction conditions minimize the energy losses. In addition to decreasing the energy losses, increasing the volume of treated wastewater is another crucial requirement of industrial applications. In this frame, the use of stacking the microbial fuel cells is a common solution while tubular and other stacked designs are being developed for practical applications. Up to date immense advances in microbial fuel cells have been recorded and the developments will continue to be able to operate at large scales with high-energy recovery. Microbial fuel cell is a unique method for the conversion of organic wastes into electricity without giving any external energy. Microbial fuel cells are capable of being modified

easily for performance improvement. It is anticipated that microbial fuel cell technology, which is in the field of interest of many disciplines such as materials science and biotechnology, will enable simultaneous wastewater treatment and sustainable energy production in the future.

References

1. Abbattista R, Ventura G, Calvano CD, Cataldi TRI, Losito I (2021) Bioactive compounds in waste by-products from olive oil production: applications and structural characterization by mass spectrometry techniques. Foods 10:1–28. https://doi.org/10.3390/foods10061236
2. Ahmad A, Buang A, Bhat AH (2016) Renewable and sustainable bioenergy production from microalgal co-cultivation with palm oil mill effluent (POME): a review. Renew Sustain Energy Rev 65:214–234. https://doi.org/10.1016/j.rser.2016.06.084
3. Ahmad T, Aadil RM, Ahmed H, Rahman U ur, Soares BCV, Souza SLQ, Pimentel TC, Scudino H, Guimarães JT, Esmerino EA, Freitas MQ, Almada RB, Vendramel SMR, Silva MC, Cruz AG (2019) Treatment and utilization of dairy industrial waste: a review. Trends Food Sci Technol 88:361–372. https://doi.org/10.1016/j.tifs.2019.04.003
4. Alzate-Gaviria L (2011) Microbial fuel cells for wastewater treatment. In: Einschlag FSG (ed) Waste water—Treatment and reutilization. InTech, pp 151–170
5. Antonopoulou G, Ntaikou I, Bebelis S, Lyberatos G (2021) On the evaluation of filtered and pretreated cheese whey as an electron donor in a single chamber microbial fuel cell. Biomass Convers Biorefinery 11:633–643. https://doi.org/10.1007/s13399-020-00653-w
6. Ashraf A, Ramamurthy R, Rene ER (2021) Wastewater treatment and resource recovery technologies in the brewery industry: current trends and emerging practices. Sustain Energy Technol Assess 47:101432. https://doi.org/10.1016/j.seta.2021.101432
7. Atallah E, Kwapinski W, Ahmad MN, Leahy JJ, Zeaiter J (2019) Effect of water-sludge ratio and reaction time on the hydrothermal carbonization of olive oil mill wastewater treatment: hydrochar characterization. J Water Process Eng 31:100813. https://doi.org/10.1016/j.jwpe.2019.100813
8. Bagheri M, Daneshvar R, Mogharei A, Vahabzadeh F (2020) Phenol-acclimated activated sludge and Ralstonia eutropha in a microbial fuel Cell for removal of olive oil from mill wastewater. Korean J Chem Eng 37:1233–1240. https://doi.org/10.1007/s11814-020-0538-x
9. Baranitharan E, Khan MR, Prasad DMR, Teo WFA, Tan GYA, Jose R (2015) Effect of biofilm formation on the performance of microbial fuel cell for the treatment of palm oil mill effluent. Bioprocess Biosyst Eng 38:15–24. https://doi.org/10.1007/s00449-014-1239-9
10. Bolzonella D, Papa M, Da Ros C, Anga Muthukumar L, Rosso D (2019) Winery wastewater treatment: a critical overview of advanced biological processes. Crit Rev Biotechnol 39:489–507. https://doi.org/10.1080/07388551.2019.1573799
11. Bose D, Sridharan S, Dhawan H, Vijay P, Gopinath M (2019) Biomass derived activated carbon cathode performance for sustainable power generation from microbial fuel cells. Fuel 236:325–337. https://doi.org/10.1016/j.fuel.2018.09.002
12. Cecconet D, Molognoni D, Callegari A, Capodaglio AG (2018) Agro-food industry wastewater treatment with microbial fuel cells: energetic recovery issues. Int J Hydrogen Energy 43:500–511. https://doi.org/10.1016/j.ijhydene.2017.07.231
13. Chandrasekhar K, Kadier A, Kumar G, Nastro RA, Jeevitha V (2018) Challenges in microbial fuel cell and future scope. In: Das D (ed). Springer International Publishing, Cham
14. Cheng YW, Chong CC, Lam MK, Leong WH, Chuah LF, Yusup S, Setiabudi HD, Tang Y, Lim JW (2021) Identification of microbial inhibitions and mitigation strategies towards cleaner bioconversions of palm oil mill effluent (POME): a review. J Clean Prod 280:124346 . https://doi.org/10.1016/j.jclepro.2020.124346

15. Chia WY, Chong YY, Chew KW, Vimali E, Jayaram M, Selvarajoo A, Muthuvelu KS, Varalakshmi P, Show PL, Arumugasamy SK (2020) Outlook on biorefinery potential of palm oil mill effluent for resource recovery. J Environ Chem Eng 8:104519. https://doi.org/10.1016/j.jece.2020.104519
16. Choudhury P, Ray RN, Bandyopadhyay TK, Basak B, Muthuraj M, Bhunia B (2021) Process engineering for stable power recovery from dairy wastewater using microbial fuel cell. Int J Hydrog Energy 46:3171–3182. https://doi.org/10.1016/j.ijhydene.2020.06.152
17. Choudhury P, Ray RN, Bandyopadhyay TK, Bhunia B (2020) Fed batch approach for stable generation of power from dairy wastewater using microbial fuel cell and its kinetic study. Fuel 266:117073. https://doi.org/10.1016/j.fuel.2020.117073
18. Civan G, Palas B, Ersöz G, Atalay S, Bavasso I, Di Palma L (2021) Experimental assessment of a hybrid process including adsorption/photo fenton oxidation and microbial fuel cell for the removal of dicarboxylic acids from aqueous solution. J Photochem Photobiol Chem 407:1–8. https://doi.org/10.1016/j.jphotochem.2020.113056
19. Colombo A, Schievano A, Trasatti SP, Morrone R, D'Antona N, Cristiani P (2017) Signal trends of microbial fuel cells fed with different food-industry residues. Int J Hydrogen Energy 42:1841–1852. https://doi.org/10.1016/j.ijhydene.2016.09.069
20. Daud NNM, Ahmad A, Yaqoob AA, Ibrahim MNM (2021) Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-021-15104-w
21. Divya Priya A, Pydi Setty Y (2019) Cashew apple juice as substrate for microbial fuel cell. Fuel 246:75–78 . https://doi.org/10.1016/j.fuel.2019.02.100
22. Dong Y, Qu Y, He W, Du Y, Liu J, Han X, Feng Y (2015) A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode. Bioresour Technol 195:66–72. https://doi.org/10.1016/j.biortech.2015.06.026
23. ElMekawy A, Hegab HM, Dominguez-Benetton X, Pant D (2013) Internal resistance of microfluidic microbial fuel cell: challenges and potential opportunities. Bioresour Technol 142:672–682. https://doi.org/10.1016/j.biortech.2013.05.061
24. Fadzli FS, Bhawani SA, Adam Mohammad RE (2021) Microbial fuel cell: recent developments in organic substrate use and bacterial electrode interaction. J Chem 2021. https://doi.org/10.1155/2021/4570388
25. Fiorentino A, Gentili A, Isidori M, Lavorgna M, Parrella A, Temussi F (2004) Olive oil mill wastewater treatment using a chemical and biological approach. J Agric Food Chem 52:5151–5154. https://doi.org/10.1021/jf049799e
26. Firdous S, Jin W, Shahid N, Bhatti ZA, Iqbal A, Abbasi U, Mahmood Q, Ali A (2018) The performance of microbial fuel cells treating vegetable oil industrial wastewater. Environ Technol Innov 10:143–151. https://doi.org/10.1016/j.eti.2018.02.006
27. Ghasemi M, Ahmad A, Jafary T, Azad AK, Kakooei S, Wan Daud WR, Sedighi M (2017) Assessment of immobilized cell reactor and microbial fuel cell for simultaneous cheese whey treatment and lactic acid/electricity production. Int J Hydrog Energy 42:9107–9115. https://doi.org/10.1016/j.ijhydene.2016.04.136
28. Gude VG (2016) Wastewater treatment in microbial fuel cells—An overview. J Clean Prod 122:287–307. https://doi.org/10.1016/j.jclepro.2016.02.022
29. Hariti M, Chemlal R, Drouiche M, Mameri N (2021) The influence of organic pollutant load and external resistance on the performance of a solid phase microbial fuel cell fed orange peel wastes. Environ Prog Sustain Energy 40:1–8. https://doi.org/10.1002/ep.13667
30. Hassan SHA, el Nasser A, Zohri A, Kassim RMF (2019) Electricity generation from sugarcane molasses using microbial fuel cell technologies. Energy 178:538–543. https://doi.org/10.1016/j.energy.2019.04.087
31. Hassan SHA, Gad El-Rab SMF, Rahimnejad M, Ghasemi M, Joo JH, Sik-Ok Y, Kim IS, Oh SE (2014) Electricity generation from rice straw using a microbial fuel cell. Int J Hydrog Energy 39:9490–9496. https://doi.org/10.1016/j.ijhydene.2014.03.259

32. Hassan SS, Williams GA, Jaiswal AK (2019) Moving towards the second generation of lignocellulosic biorefineries in the EU: drivers, challenges, and opportunities. Renew Sustain Energy Rev 101:590–599. https://doi.org/10.1016/j.rser.2018.11.041
33. He J, Xin X, Pei Z, Chen L, Chu Z, Zhao M, Wu X, Li B, Tang X, Xiao X (2021) Microbial profiles associated improving bioelectricity generation from sludge fermentation liquid via microbial fuel cells with adding fruit waste extracts. Bioresour Technol 337:125452. https://doi.org/10.1016/j.biortech.2021.125452
34. Heilmann J, Logan BE (2006) Production of electricity from proteins using a microbial fuel cell. Water Environ Res 78:531–537. https://doi.org/10.2175/106143005x73046
35. Hu H, Li X, Wu S, Yang C (2020) Sustainable livestock wastewater treatment via phytoremediation: current status and future perspectives. Bioresour Technol 315:123809 . https://doi.org/10.1016/j.biortech.2020.123809
36. Ioannou LA, Puma GL, Fatta-Kassinos D (2015) Treatment of winery wastewater by physicochemical, biological and advanced processes: a review. J Hazard Mater 286:343–368. https://doi.org/10.1016/j.jhazmat.2014.12.043
37. Islam MA, Woon CW, Ethiraj B, Cheng CK, Yousuf A, Khan MMR (2017) Correlation of power generation with time-course biofilm architecture using Klebsiella variicola in dual chamber microbial fuel cell. Int J Hydrog Energy 42:25933–25941. https://doi.org/10.1016/j.ijhydene.2017.08.193
38. Jadhav DA, Jain SC, Ghangrekar MM (2016) Cow's urine as a yellow gold for bioelectricity generation in low cost clayware microbial fuel cell. Energy 113:76–84. https://doi.org/10.1016/j.energy.2016.07.025
39. Jalilnejad Falizi N, Güngören Madenoğlu T, Kukul Kurttaş Y, Meriç K, Gürgülü H, Özçakal E, Cengiz Üremek N, Ballice L, Yüksel M, Sağlam M, Kabay N (2020) Production of biodiesel from safflower plant cultivated using membrane bioreactor (MBR) effluent discharged from wastewater treatment plant. J Chem Technol Biotechnol 95:527–534. https://doi.org/10.1002/jctb.6237
40. Janet Joshiba G, Senthil Kumar P, Femina CC, Jayashree E, Racchana R, Sivanesan S (2019) Critical review on biological treatment strategies of dairy wastewater. Desalin Water Treat 160:94–109. https://doi.org/10.5004/dwt.2019.24194
41. Jiao Y, Hu Y, Han L, Zhou M (2020) Activated carbon derived from rice husk as efficient oxygen reduction catalyst in microbial fuel cell. Electroanalysis 32:2969–2975. https://doi.org/10.1002/elan.202060409
42. Jiménez-Tototzintle M, Oller I, Hernández-Ramírez A, Malato S, Maldonado MI (2015) Remediation of agro-food industry effluents by biotreatment combined with supported TiO_2/H_2O_2 solar photocatalysis. Chem Eng J 273:205–213. https://doi.org/10.1016/j.cej.2015.03.060
43. Karthikeyan R, Wang B, Xuan J, Wong JWC, Lee PKH, Leung MKH (2015) Interfacial electron transfer and bioelectrocatalysis of carbonized plant material as effective anode of microbial fuel cell. Electrochim Acta 157:314–323. https://doi.org/10.1016/j.electacta.2015.01.029
44. Kebaili H, Kameche M, Innocent C, Ziane FZ, Sabeur SA, Sahraoui T, Ouis M, Zerrouki A, Charef MA (2021) Treatment of fruit waste leachate using microbial fuel cell: preservation of agricultural environment. Shengtai Xuebao/Acta Ecol Sin 41:97–105. https://doi.org/10.1016/J.CHNAES.2020.09.004
45. Kolev S (2017) General characteristics and treatment possibilities of dairy wastewater—A review. Food Technol Biotechnol 53:237–242
46. Kondaveeti S, Mohanakrishna G, Kumar A, Lai C, Lee JK, Kalia VC (2019) Exploitation of citrus peel extract as a feedstock for power generation in microbial fuel cell (MFC). Indian J Microbiol 59:476–481. https://doi.org/10.1007/s12088-019-00829-7
47. Kugarajah V, Dharmalingam S (2021) Effect of silver incorporated sulphonated poly ether ether ketone membranes on microbial fuel cell performance and microbial community analysis. Chem Eng J 415:128961. https://doi.org/10.1016/j.cej.2021.128961

48. Lai MF, Lou CW, Lin JH (2018) Improve 3D electrode materials performance on electricity generation from livestock wastewater in microbial fuel cell. Int J Hydrog Energy 43:11520–11529. https://doi.org/10.1016/j.ijhydene.2017.06.047
49. Lee ZS, Chin SY, Lim JW, Witoon T, Cheng CK (2019) Treatment technologies of palm oil mill effluent (POME)and olive mill wastewater (OMW): a brief review. Environ Technol Innov 15:100377. https://doi.org/10.1016/j.eti.2019.100377
50. Li F, An X, Wu D, Xu J, Chen Y, Li W, Cao Y, Guo X, Lin X, Li C, Liu S, Song H (2019) Engineering microbial consortia for high-performance cellulosic hydrolyzates-fed microbial fuel cells. Front Microbiol 10:1–10. https://doi.org/10.3389/fmicb.2019.00409
51. Li M, Zhou M, Tian X, Tan C, Gu T (2021) Enhanced bioenergy recovery and nutrient removal from swine wastewater using an airlift-type photosynthetic microbial fuel cell. Energy 226:120422. https://doi.org/10.1016/j.energy.2021.120422
52. Li M, Zhou M, Tian X, Tan C, McDaniel CT, Hassett DJ, Gu T (2018) Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity. Biotechnol Adv 36:1316–1327. https://doi.org/10.1016/j.biotechadv.2018.04.010
53. Liu J, Vipulanandan C (2017) Effects of Fe, Ni, and Fe/Ni metallic nanoparticles on power production and biosurfactant production from used vegetable oil in the anode chamber of a microbial fuel cell. Waste Manag 66:169–177. https://doi.org/10.1016/j.wasman.2017.04.004
54. Liu T, Nadaraja AV, Friesen J, Gill K, Lam MI, Roberts DJ (2021) Narrow pH tolerance found for a microbial fuel cell treating winery wastewater. J Appl Microbiol 131:2280–2293. https://doi.org/10.1111/jam.15102
55. Lu M, Chen S, Babanova S, Phadke S, Salvacion M, Mirhosseini A, Chan S, Carpenter K, Cortese R, Bretschger O (2017) Long-term performance of a 20-L continuous flow microbial fuel cell for treatment of brewery wastewater. J Power Sour 356:274–287. https://doi.org/10.1016/j.jpowsour.2017.03.132
56. Ma D, Jiang ZH, Lay CH, Zhou D (2016) Electricity generation from swine wastewater in microbial fuel cell: hydraulic reaction time effect. Int J Hydrog Energy 41:21820–21826. https://doi.org/10.1016/j.ijhydene.2016.08.019
57. Malekmohammadi S, Mirbagheri SA (2021) A review of the operating parameters on the microbial fuel cell for wastewater treatment and electricity generation. Water Sci Technol 84:1309–1323. https://doi.org/10.2166/wst.2021.333
58. Malvis A, Hodaifa G, Halioui M, Seyedsalehi M, Sánchez S (2019) Integrated process for olive oil mill wastewater treatment and its revalorization through the generation of high added value algal biomass. Water Res 151:332–342. https://doi.org/10.1016/j.watres.2018.12.026
59. Marassi RJ, Queiroz LG, Silva DCVR, dos Santos FS, Silva GC, de Paiva TCB (2020) Long-term performance and acute toxicity assessment of scaled-up air-cathode microbial fuel cell fed by dairy wastewater. Bioprocess Biosyst Eng 43:1561–1571. https://doi.org/10.1007/s00449-020-02348-y
60. Michalopoulos I, Chatzikonstantinou D, Mathioudakis D, Vaiopoulos I, Tremouli A, Georgiopoulou M, Papadopoulou K, Lyberatos G (2017) Valorization of the liquid fraction of a mixture of livestock waste and cheese whey for biogas production through high-rate anaerobic Co-digestion and for electricity production in a microbial fuel cell (MFC). Waste Biomass Valoriz 8:1759–1769. https://doi.org/10.1007/s12649-017-9974-1
61. Moharir PV, Tembhurkar AR (2018) Effect of recirculation on bioelectricity generation using microbial fuel cell with food waste leachate as substrate. Int J Hydrog Energy 43:10061–10069. https://doi.org/10.1016/j.ijhydene.2018.04.072
62. Moradian JM, Fang Z, Yong YC (2021) Recent advances on biomass-fueled microbial fuel cell. Bioresour Bioprocess 8. https://doi.org/10.1186/s40643-021-00365-7
63. Moravvej Z, Makarem MA, Rahimpour MR (2019) The fourth generation of biofuel. Elsevier Inc.
64. Naina Mohamed S, Thomas N, Tamilmani J, Boobalan T, Matheswaran M, Kalaichelvi P, Alagarsamy A, Pugazhendhi A (2020) Bioelectricity generation using iron(II) molybdate nanocatalyst coated anode during treatment of sugar wastewater in microbial fuel cell. Fuel 277:118119. https://doi.org/10.1016/j.fuel.2020.118119

65. Nath A, Mishra A, Pande PP (2019) A review natural polymeric coagulants in wastewater treatment. Mater Today Proc 46:6113–6117. https://doi.org/10.1016/j.matpr.2020.03.551
66. Negassa LW, Mohiuddin M, Tiruye GA (2021) Treatment of brewery industrial wastewater and generation of sustainable bioelectricity by microbial fuel cell inoculated with locally isolated microorganisms. J Water Process Eng 41:102018. https://doi.org/10.1016/j.jwpe.2021.102018
67. Nwaokocha CN, Giwa SO, Layeni AT, Kuye SI, Samuel OD, Ogunbona CK, Adebayo JK, Sosanya A, Babalola A (2021) Microbial fuel cell: bio-energy production from Nigerian corn starch wastewater using iron electrodes. Mater Today Proc 46:5565–5569. https://doi.org/10.1016/j.matpr.2020.09.345
68. Obileke KC, Onyeaka H, Meyer EL, Nwokolo N (2021) Microbial fuel cells, a renewable energy technology for bio-electricity generation: a mini-review. Electrochem commun 125:107003. https://doi.org/10.1016/j.elecom.2021.107003
69. Ochando-Pulido JM, Pimentel-Moral S, Verardo V, Martinez-Ferez A (2017) A focus on advanced physico-chemical processes for olive mill wastewater treatment. Sep Purif Technol 179:161–174. https://doi.org/10.1016/j.seppur.2017.02.004
70. Oliveira VB, Simões M, Melo LF, Pinto AMFR (2013) A 1D mathematical model for a microbial fuel cell. Energy 61:463–471. https://doi.org/10.1016/j.energy.2013.08.055
71. Othman I, Anuar AN, Ujang Z, Rosman NH, Harun H, Chelliapan S (2013) Livestock wastewater treatment using aerobic granular sludge. Bioresour Technol 133:630–634. https://doi.org/10.1016/j.biortech.2013.01.149
72. Pal M, Sharma RK (2020) Development of wheat straw based catholyte for power generation in microbial fuel cell. Biomass Bioenergy 138:105591. https://doi.org/10.1016/j.biombioe.2020.105591
73. Palanisamy G, Jung HY, Sadhasivam T, Kurkuri MD, Kim SC, Roh SH (2019) A comprehensive review on microbial fuel cell technologies: processes, utilization, and advanced developments in electrodes and membranes. J Clean Prod 221:598–621. https://doi.org/10.1016/j.jclepro.2019.02.172
74. Pandit S, Savla N, Sonawane JM, Sani AM, Gupta PK, Mathuriya AS, Rai AK, Jadhav DA, Jung SP, Prasad R (2021) Agricultural waste and wastewater as feedstock for bioelectricity generation using microbial fuel cells: recent advances. Fermentation 7. https://doi.org/10.3390/fermentation7030169
75. Penteado ED, Fernandez-Marchante CM, Zaiat M, Gonzalez ER, Rodrigo MA (2017) Influence of carbon electrode material on energy recovery from winery wastewater using a dual-chamber microbial fuel cell. Environ Technol (United Kingdom) 38:1333–1341. https://doi.org/10.1080/09593330.2016.1226961
76. Pepè Sciarria T, de Oliveira MAC, Mecheri B, D'Epifanio A, Goldfarb JL, Adani F (2020) Metal-free activated biochar as an oxygen reduction reaction catalyst in single chamber microbial fuel cells. J Power Sour 462. https://doi.org/10.1016/j.jpowsour.2020.228183
77. Pepe Sciarria T, Merlino G, Scaglia B, D'Epifanio A, Mecheri B, Borin S, Licoccia S, Adani F (2015) Electricity generation using white and red wine lees in air cathode microbial fuel cells. J Power Sourc 274:393–399. https://doi.org/10.1016/j.jpowsour.2014.10.050
78. Pepé Sciarria T, Tenca A, D'Epifanio A, Mecheri B, Merlino G, Barbato M, Borin S, Licoccia S, Garavaglia V, Adani F (2013) Using olive mill wastewater to improve performance in producing electricity from domestic wastewater by using single-chamber microbial fuel cell. Bioresour Technol 147:246–253. https://doi.org/10.1016/j.biortech.2013.08.033
79. Rajagopal R, Saady NMC, Torrijos M, Thanikal JV, Hung YT (2013) Sustainable agro-food industrial wastewater treatment using high rate anaerobic process. Water (Switzerland) 5:292–311. https://doi.org/10.3390/w5010292
80. Raychaudhuri A, Behera M (2020) Ceramic membrane modified with rice husk ash for application in microbial fuel cells. Electrochim Acta 363:137261. https://doi.org/10.1016/j.electacta.2020.137261
81. Raychaudhuri A, Behera M (2021) Enhancement of bioelectricity generation by integrating acidogenic compartment into a dual-chambered microbial fuel cell during rice mill wastewater treatment. Process Biochem 105:19–26. https://doi.org/10.1016/j.procbio.2021.03.003

82. Sarmin S, Tarek M, Roopan SM, Cheng CK, Rahman Khan MM (2021) Significant improvement of power generation through effective substrate-inoculum interaction mechanism in microbial fuel cell. J Power Sour 484:229285. https://doi.org/10.1016/j.jpowsour.2020.229285
83. Sedighi M, Aljlil SA, Alsubei MD, Ghasemi M, Mohammadi M (2018) Performance optimisation of microbial fuel cell for wastewater treatment and sustainable clean energy generation using response surface methodology. Alex Eng J 57:4243–4253. https://doi.org/10.1016/j.aej.2018.02.012
84. Sekar AD, Jayabalan T, Muthukumar H, Chandrasekaran NI, Mohamed SN, Matheswaran M (2019) Enhancing power generation and treatment of dairy waste water in microbial fuel cell using Cu-doped iron oxide nanoparticles decorated anode. Energy 172:173–180. https://doi.org/10.1016/j.energy.2019.01.102
85. Serrano L, de la Varga D, Ruiz I, Soto M (2011) Winery wastewater treatment in a hybrid constructed wetland. Ecol Eng 37:744–753. https://doi.org/10.1016/j.ecoleng.2010.06.038
86. Shen J, Wang C, Liu Y, Hu C, Xin Y, Ding N, Su S (2018) Effect of ultrasonic pretreatment of the dairy manure on the electricity generation of microbial fuel cell. Biochem Eng J 129:44–49. https://doi.org/10.1016/j.bej.2017.10.013
87. Shen R, Liu Z, He Y, Zhang Y, Lu J, Zhu Z, Si B, Zhang C, Xing XH (2016) Microbial electrolysis cell to treat hydrothermal liquefied wastewater from cornstalk and recover hydrogen: degradation of organic compounds and characterization of microbial community. Int J Hydrog Energy 41:4132–4142. https://doi.org/10.1016/j.ijhydene.2016.01.032
88. Shi W, Healy MG, Ashekuzzaman SM, Daly K, Leahy JJ, Fenton O (2021) Dairy processing sludge and co-products: a review of present and future re-use pathways in agriculture. J Clean Prod 314:128035. https://doi.org/10.1016/j.jclepro.2021.128035
89. Simate GS, Cluett J, Iyuke SE, Musapatika ET, Ndlovu S, Walubita LF, Alvarez AE (2011) The treatment of brewery wastewater for reuse: state of the art. Desalination 273:235–247. https://doi.org/10.1016/j.desal.2011.02.035
90. Sivakumar D (2021) Wastewater treatment and bioelectricity production in microbial fuel cell: salt bridge configurations. Int J Environ Sci Technol 18:1379–1394. https://doi.org/10.1007/s13762-020-02864-0
91. Song TS, Zhang J, Hou S, Wang H, Zhang D, Li S, Xie J (2018) In situ electrokinetic remediation of toxic metal-contaminated soil driven by solid phase microbial fuel cells with a wheat straw addition. J Chem Technol Biotechnol 93:2860–2867. https://doi.org/10.1002/jctb.5638
92. Syed Z, Sonu K, Sogani M (2021) Cattle manure management using microbial fuel cells for green energy generation. Biofuels Bioprod Biorefining, 1–11. https://doi.org/10.1002/bbb.2293
93. Tajdid Khajeh R, Aber S, Nofouzi K, Ebrahimi S (2020) Treatment of mixed dairy and dye wastewater in anode of microbial fuel cell with simultaneous electricity generation. Environ Sci Pollut Res 27:43711–43723. https://doi.org/10.1007/s11356-020-10232-1
94. Tamboli E, Eswari JS (2018) Microbial fuel cell configurations: an overview. Elsevier, B.V
95. Tee PF, Abdullah MO, Tan IAW, Mohamed Amin MA, Nolasco-Hipolito C, Bujang K (2016) Performance evaluation of a hybrid system for efficient palm oil mill effluent treatment via an air-cathode, tubular upflow microbial fuel cell coupled with a granular activated carbon adsorption. Bioresour Technol 216:478–485. https://doi.org/10.1016/j.biortech.2016.05.112
96. Toczyłowska-Mamińska R, Szymona K, Król P, Gliniewicz K, Pielech-Przybylska K, Kloch M, Logan BE (2018) Evolving microbial communities in cellulose-fed microbial fuel cell. Energies 11:1–12. https://doi.org/10.3390/en11010124
97. Tsagaraki E, Lazarides HN, Petrotos KB, Olive Mill wastewater treatment. In: Oreopoulou V, Russ W (eds) Utilization of by-products and treatment of waste in the food industry. Springer, US, Boston, pp 133–157
98. Umar MF, Rafatullah M, Abbas SZ, Mohamad Ibrahim MN, Ismail N (2021) Enhanced benzene bioremediation and power generation by double chamber benthic microbial fuel cells fed with sugarcane waste as a substrate. J Clean Prod 310:127583. https://doi.org/10.1016/j.jclepro.2021.127583

99. Varanasi JL, Das D (2018) Bioremediation and power generation from organic wastes using microbial fuel cell. In: Das D (ed) Microbial fuel cell. Springer International Publishing, Cham, pp 285–306
100. Venkata Mohan S, Velvizhi G, Annie Modestra J, Srikanth S (2014) Microbial fuel cell: critical factors regulating bio-catalyzed electrochemical process and recent advancements. Renew Sustain Energy Rev 40:779–797. https://doi.org/10.1016/j.rser.2014.07.109
101. Vilas Boas J, Oliveira VB, Marcon LRC, Simões M, Pinto AMFR (2019) Optimization of a single chamber microbial fuel cell using Lactobacillus pentosus: influence of design and operating parameters. Sci Total Environ 648:263–270. https://doi.org/10.1016/j.scitotenv.2018.08.061
102. Wang Y, Serventi L (2019) Sustainability of dairy and soy processing: a review on wastewater recycling. J Clean Prod 237:117821. https://doi.org/10.1016/j.jclepro.2019.117821
103. Wu CH, Liu SH, Chu HL, Li YC, Lin CW (2017) Feasibility study of electricity generation and organics removal for a molasses wastewater by a waterfall-type microbial fuel cell. J Taiwan Inst Chem Eng 78:150–156. https://doi.org/10.1016/j.jtice.2017.05.019
104. Xie B, Gong W, Ding A, Yu H, Qu F, Tang X, Yan Z, Li G, Liang H (2017) Microbial community composition and electricity generation in cattle manure slurry treatment using microbial fuel cells: effects of inoculum addition. Environ Sci Pollut Res 24:23226–23235. https://doi.org/10.1007/s11356-017-9959-4
105. Xin S, Shen J, Liu G, Chen Q, Xiao Z, Zhang G, Xin Y (2020) High electricity generation and COD removal from cattle wastewater in microbial fuel cells with 3D air cathode employed non-precious Cu_2O/reduced graphene oxide as cathode catalyst. Energy 196:117123. https://doi.org/10.1016/j.energy.2020.117123
106. Yuvraj C, Aranganathan V (2018) Configuration analysis of stacked microbial fuel cell in power enhancement and its application in wastewater treatment. Arab J Sci Eng 43:101–108. https://doi.org/10.1007/s13369-017-2720-y
107. Zhang N, Liu W, Peng Y, Song X (2021) Anaerobic membrane bioreactors for livestock wastewater treatment and resource recovery: opportunities and challenges. Curr Pollut Reports 7:277–285. https://doi.org/10.1007/s40726-021-00192-6
108. Żyłka R, Karolinczak B, Dąbrowski W (2021) Structure and indicators of electric energy consumption in dairy wastewater treatment plant. Sci Total Environ 782. https://doi.org/10.1016/j.scitotenv.2021.146599

Removal of Phenolic Compound from Wastewater Using Microbial Fuel Cells

N. Hemashenpagam and S. Selvajeyanthi

Abstract Adverse changes in the natural environment caused by any form of contaminants are known as pollution. Industrial effluent is one of the major sources for water pollution and is a matter of great concern, because of its threat to aquatic life. Phenolic compounds are moderately water-soluble pollutants generated in various Industries. They are considered as priority pollutants in water by EPA and NPRI in USA and Canada. Industrial effluent containing phenols and their derivatives are profoundly toxic to humans, animals, aquatic ecosystems, and indigenous microbiota. Conventional methods of physical and chemical treatment are ineffective. The biological approach of wastewater treatment is a promising technology of microbial fuel cells degrades phenolic compounds in both aerobic and anaerobic pathways, the harvest energy of bioelectricity achieved. Microbial fuel cell technology is environmentally friendly and employs bioelectrochemical catalytic activity of microbes to produce biocurrent from wastewater containing phenolic compounds. It has a tremendous advantage: the most convenient method of removing phenolic compounds by bio-treatment is highly established and successful method inexpensive safe, easy to operate and environment-friendly.

Keywords Water pollution · Phenolic compounds · Biodegradation · Wastewater treatment · Microbial fuel cells · Bioelectricity

N. Hemashenpagam (✉)
Department of Microbiology, Hindusthan College of Arts and Science, Coimbatore 641028, Tamilnadu, India
e-mail: hemashenpagam.n@hicas.ac.in

S. Selvajeyanthi
Department of Microbiology, Shri Nehru Maha Vidyalaya College of Arts and Science, Coimbatore 641050, Tamilnadu, India

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_14

1 Introduction

Currently witnessing a worldwide strength shift as a result of increasing energy demands and limited supply. Major parts of non-renewable energy sources are exhausting and Renewable energy sources are not being used properly. Prospective attention is needed for research into alternative energy generation and creating a clean environment through reduction of contaminants. The rapid urbanization and industrialization releases a lot of potential contaminants. Industry utilizes a variety of chemicals as a raw material for production of plastic, paper, food, toys, pharmaceuticals, dyes, pigments, and aromatic compounds that were widely employed for a variety of uses, including textiles, printing, and cosmetics. The known fact is that a lot of untreated and inefficiently treated wastewater is dumped into the environment, which is dangerous to the ecological system.

1.1 Water Pollution

Water pollution is a notable problem in the atmosphere, which expresses a risk to humans and the environment. Water poisoning by toxic pollutants can cause acute (death) and chronic toxicity (neurological issues) and also leads to carcinogenicity. Water pollution is the poisoning of water sources by substances that make the water hazardous for drinking, cooking, cleaning, swimming, and other activities. Pollutants involve chemicals, trash, bacteria, parasites and ultimately make their way to the water [1].

The depletion of fossil fuels, ecological contamination, and the necessity for scientific innovations to provide hygienic water and renewable energy burdens the current society. The policymakers and scientists recently intensified concern about exposure to chemical compounds that the environment affects humans and wildlife, particularly the aquatic environment. In measured concern about phenolic compounds this regards as they tend to be dumped in the environment over a period of time accumulated; this leads to expel as waste deleterious toxic effects on humans and aquatic animals.

The most important ecological problem created by inadequate treated industrial effluent invades main water supplies. Accumulation of pollutants in the atmosphere and toxic removal processing is of special importance. Currently various approaches like physical, chemical and biological methods are available, for example chemical methods include precipitation, coagulation, flocculation, membrane filtration, adsorption and electrochemical technologies [2]. In an attempt to make sewage treatment or removal of toxic from water, these physical and chemical both are cost effective, and a lot of consideration has to be made for promote novel approach to cleaning and recovery of chemicals and metals[3]. Prospective attention to biological approach is sustainable and expensively adoptable.

Phenolic compounds (PCs) are by-products of various industrial processes in manufacturing of dyes, plastics, drugs, antioxidants, papers, petroleum industries, fertilizers, surfactants, explosives, textiles, rubbers, plastics curing agents, and antioxidants. For example, polymer manufacturers use PCs for manufacturing of thermosetting polymers like bakelite, plywood, adhesives, polyester, polyols, and corrosion-resistant polyesters. Phenols, phenolic resins, and phenolic compounds are liberated with the effluent from different kinds of industries such as the textile industry, woolen mills, dye industries, paper industries, steel plants, petrochemical industries, paint industries, oil, drilling and gas extraction units, pharmaceuticals, coal washeries, and refractory industries [4–6]. PCs are employed in various applications in the pharmaceuticals industry which are used as germicides because of their protein denaturation ability. Food industries are also using PCs for packing to increase the shelf period of the things and to assist in maintaining quality, sensible characteristics, and food safety [7].

These effluents produce irritation odor and taste difficulties and are venomous even at low concentrations. However, under particular environmental circumstances, some PCs are susceptive to have major threats to public health, negative impacts on humans and living organisms [8]. The high solubility nature and volatility exposure to PCs in water can lead to further formation of hazardous by-products during chemical treatment processes via nasal, oral, eye, skin/dermal contact can create chronic damages, even make eventual death with higher levels of exposure. PCs are significantly harmful due to mutagenic and carcinogenic toxicity effects that have been directly and tribute to environmental conditions and health impacts on humans and living organisms [8, 9].

Some phenolic compounds are listed as a priority pollutant due to the toxicity and environmental concerns by the United States Environmental Protection Agency (USEPA) and European Commission (EC). Phenols are general environmental pollutants obtained in potable water, soil, and ambient air. For example, chlorophenol is known for its toxicity, carcinogenicity, and persistence in the atmosphere (CPCB 2016). The elimination of PCs from aqueous body has become an integral component of environmental perceptivity, and a number of technologies have been proposed to remove PCs from aqueous streams [8, 10].

2 Phenol

In phenol, the −OH group is directly attached to an aromatic ring and is designated as ArOH. Phenols are widely used as an antiseptic and disinfectant. It is a useful precursor for the synthesis of food preservatives, pharmaceuticals, resins, polymers, and adhesives. Bisphenol A is a component of polycarbonate plastics.

The Phenolics are aromatic compounds with single or multiple aromatic rings connected to one or more hydroxyl groups. Phenolics are naturally occurring chemical substances in many biological systems and present as flavoring agents, neurotransmitters, and vitamins. With over 8000 identified structures of phenolics were the most common secondary plant metabolites. They differ from simple phenolics, such as phenolic acids and complex combinations, such as tannins. Plants are protected by the composites from ultraviolet (UV), diseases, and several predators. Because they are found in all plant organs, they are a crucial part of the human diet (Shah et al. 2018; Balasundram et al. 2006).

2.1 Classification of Phenolic Compounds

Phenol is a benzene derivative, consisting of phenyl (−C6H5) bonded to a hydroxyl (−OH) group. Phenol (C6H5OH) and its derivative are collectively named phenolic compounds (PCs), possessing an aromatic ring joined to one or more hydroxyl groups. The variety of groups of chemical substances commonly being in many living tissues of plants and also synthesized at lower concentrations by microorganisms [11, 12]. Similarly many synthesized phenolic compounds are used for a variety of domestic and industrial applications. These compounds can be categorized according to Harborne and Simmonds into groups based on the number of carbons in the molecule ranging from the monomers; the simple replaced PC consisting of the parental phenol linked to one or two more other functional groups such as cyaninlignans, neolignan dimers/oligomers, lignin polymers, tannin oligomers and polymers, flavanols, quinones, phlobaphenes, and polymers [9]. The common structure of simple PC and nomenclature patterns are given in Fig. 1 with R, R1, and R2 as generic substituents [11].

3 Effect of Phenolic Pollution on the Environment

The overutilization of phenol and derivatives in different industrial sectors may disturb the ecosystem by the release of industrial effluent containing phenolic compounds, which can exert severe and aggressive effects on the ecosystem as well as humans and aquatic life. The concentration of PC in the surface water is reflected sensitively by the type of industrial source processes [6] (Michalowicz and Duda 2004).

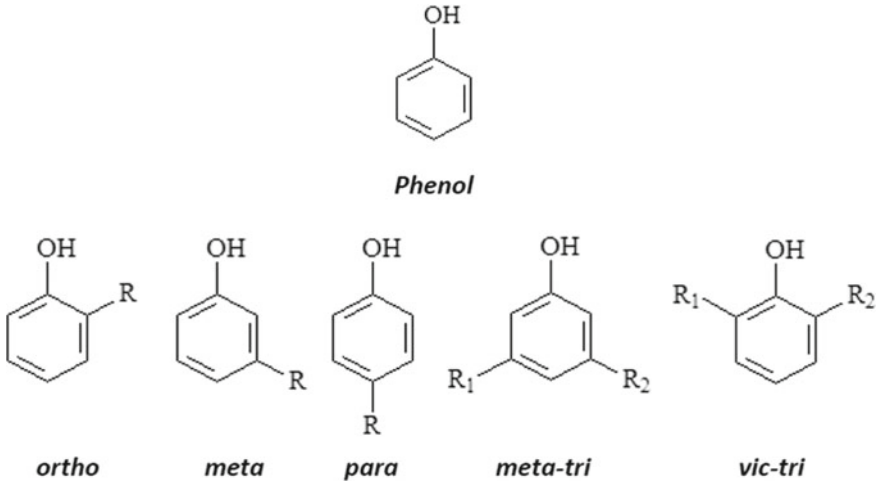

Fig. 1 Structure and nomenclature for phenol and substitution patterns of phenolic compounds. *Source* Mu'azu et al. [10]. @MDPI

3.1 Natural Source

Phenol is produced by the normal degradation of organic decays including Benzene which is a dominant metabolite of benzene that exists widely in the atmosphere [13]; hence phenol may be produced in natural degradation of benzene, when increased environmental level is the main cause of forest fire.

Phenols are identified within the volatile mixtures from liquid compost. Decomposing vegetation of wood generates various phenols as the benzene with the hydroxyl group is a most important part of a woody substance called Lignin. Paper industries will eliminate lignin in-process paper produced from trees and degrade to form abundant substances including phenols (CPCB 2016).

3.2 Anthropogenic Sources

Phenyl is the primary feedstock in which several commercially important substances are made including phenolic resins, bisphenol-A, caprolactam, alkylphenol, in addition to chlorophenol such as pentachlorophenol [14]. Phenolic resins are utilized as a binding material in insulation material, chipboard and triplex, paints, and casting sand foundries; 2–3% of contents may differ from insulin relation material to >50% for Molds. The ejection is proportional to the concentration of free phenol which is present as a monomer in these materials approximately 1–5%. In addition, thermal breakdown of resins will release phenol, the phenol emissions develop both during the production of molds, kernels and during founding, which may be liberated into

the air [15]. Production of phenols and phenol derivatives, caprolactam, cokes, insulation material, Process emissions, emission to water also results from processing and incineration of the woods such as home fires, wood-burning may include extensive quantities of phenol. The potential origin of phenol is the atmospheric decay of benzene under the influence of light. Phenol has been noticed in smoke foods also (CPCB 2016). PCs are found in effluents from coal gasification, coke-oven batteries, refinery and electrochemical plants, and other industries, such as synthetic chemicals, herbicides, pesticides, antioxidants, paper industry, photo developing chemicals, etc. [16]. PCs have considerable allelopathic appliance in agriculture and forestry as herbicides, insecticides, and fungicides (Zhao et al. 2010; CPCB 2006). The impacts of phenolic compounds in wastewater on aquatic habitats have been examined. PCs act as inhibitory substances from the growth of aquatic lives and suppress the growth of microalgal [17].

The effects of phenolic compounds in wastewater on aquatic habitats have been analyzed and emerging contaminants of PCs perform as inhibitory substances for development of aquatic life and suppressing algal growth. PCs are intermediate and by-products of water chlorination and a priority pollutant of the aquatic environment; Chinese aquatic systems investigated the potential hazards of chlorophenol such as dichlorophenol, trichlorophenol, and pentachlorophenol [18]. Nitrophenols are water-soluble compounds. Nitrophenols are toxic to the embryo and early life stage of fish; embryotoxicity and teratogenicity have been observed in zebrafish (Daniorerio) with toxicity of 2-nitrophenol and 2,4 dinitrophenol [19]. Chlorophenol is deadly and related mechanism in fish is likely to spoil DNA pathways and disturb endocrine function leading to cell death. For example, embryotoxicity of 2,4dichlorophenol is highly disturbing for thyroid hormones of both embryos and adult fish on rare fish *Gobiocyprisrarus* [20, 21]. PC does not naturally degrade and it can collect in tissues, cells and organs again interfere via different routes or by food chain. The compounds can further lead to acute or chronic effects on aquatic systems; therefore, removal of its compounds should be attained to decrease the harmful effect on aquatic organisms.

3.3 Toxicity of Phenol and Phenolic Compounds and Mechanism of Action

Phenol toxicity is related to two main processes: specific toxicity and unspecified toxicity. Unspecified toxicity, hydrophobicity of single compound, and production of free radicals will alter the solubility of phenol in a cell fractions and interactions of the compound with specified cell and tissue. For example, the increase of hydrophobicity of chlorophenol is related to increasing number of chlorine atoms that enhances toxicity. The permissible level of phenol is restricted to 1 PPB in surface water [13]. The hazardous phenolic compounds in industry effluents are 2-Methylphenol

(cresol), 4-chloro-2-methylphenol, 2,4-dinitrophenol, and phenols which act as a harmful pollutant even at low concentrations in water [22].

Toxic influence of organic compounds depends on several factors. The penetration of phenol in organisms is associated with the penetration of compounds across cell membranes and strongly affects diffusion in hydrophobicity. The raises in hydrophobicity affect more effectively the diffusion of cell membrane by phenol and therefore increase the toxicity of xenobiotics. PCs are oxidative substrates and donate free electrons that will react with molecules. Naturally, one electron reaction in a cell is frequently catalyzed by oxidative peroxidase enzymes present in liver lungs and other organs. Phenoxy radicals and intermediate metabolites interact with biomolecules and form hydrogen peroxide or superoxide radicals. The cause of these forms on specific cell structure depends on phenol reactivity.

Higher activity of phenols undergoes radical reactions and leads to lipid peroxidation of cell membrane; the lower activity leads to cell damage of endoplasmic reticulum mitochondria and nucleus. Toxicity of PCs is based on a kind of phenolic substrate reaction and also localization in cell and phase of cell production. PCs systemic toxicity causes severe and long-lasting effects on aquatic life and humans (CPCB 2006).

The case study of a nine-year-old girl was exposed to Creolin disinfectant containing phenol resulting in systemic toxicity. Phenolic toxicity includes hypertension, metabolic acidosis, renal failure and causes injuries in the gastrointestinal tract. Chronic phenol exposure may lead to kidney damage, eye and skin discoloration (David et al. 2015) The PCs in wastewater enter into the aquatic organisms and fish bodies and effects metabolism, survival, growth, reproductive potential, and unpredictable changes in aquatic life and also the population of phytoplankton is reduced [23].

Phenol and its derivatives can cause deflocculation. Removal of phenol by conventional physicochemical treatment is ineffective and additional use of chemicals leads to formation of toxic by-products and its cost effectiveness; biological treatment appears to be a good solution [24]. The biological effects of PCs are varied with type, position, and number of substitutions on the parent molecule. Phenolics affects the feeding rate of fish, oxygen consumption rate, and ATP formation. Aspects of behavior are affected, and intoxication leads to death of some of the fish and invertebrates in aquatic ecosystems. More than 25 mg/L of phenol level affects fish embryo survival. Amphibians were sensitive to 0.5 mg/L. The 1.74 mg/L of pentachlorophenol inhibits the fish growth; affects blood glucose, blood lactate levels, immunoglobulin levels, blood protein level, and tissues. The hemorrhaging, oedema, and blood infiltration were common effects observed in fish at 4 mg/L of phenol. 12.5 mg/L of PCs can reduce the level of neurohormones within 10 days of exposure (Arthur et al. 1979). When exposed chronically to phenol of 2.85 and 4.11 mg/L, it causes reduction of primary productivity, phytoplankton, dissolved oxygen, and zooplankton of aquatic systems [23].

4 Treatment of Phenolic Compounds From Environment

Phenolic compounds are the main priority contaminants accumulated in aquatic systems, due to high toxicity even at low concentration affects the living things, and the treatment of such wastewater impacts the lives of aquatic systems. PCs are removed by physicochemical and biological treatments. The conventional treatments are adsorption, membrane process, reverse osmosis, nanofiltration, extraction, distillation, chemical oxidation, electrochemical oxidation and fenton like treatment; research is carried out with new technologies such as wet air oxidation, catalytic wet air oxidation, solvent-based extraction, photocatalytic membrane reactors, forward osmosis and membrane aromatic recovery system. But due to large quantities and high energy cost, biological treatment as mentioned is environmentally friendly, simple design, and energy-saving. Nowadays, growing interest is in biological treatment of PCs with enzymatic treatment and microbial fuel cells. Bioelectrochemical systems of Microbial Electrochemical Technologies (MET) present novel method for sewage treatment; recent research at invitro level explains extraordinary outcomes results in pollutants discharge. MET is classified based on the application as follows [25].

S. No	Electrochemical technology	Applications
1	Microbial fuel cells (MFC)	Production of electric current
2	Microbial electrolysis cells (MEC)	H_2 synthesis
3	Microbial desalination cell (MDC)	Water desalination
4	Microbial remediation cell (MRC)	Cathode reduction of oxidized pollutants

Bacteria generate electricity through the substrate oxidation process, for example, *Escherichia coli.*

5 Degradation of Phenol Through Aerobic and Anaerobic Pathways

Microbial fuel cell is used for sewage treatment and power recovery. Both aerobic and anaerobic microbial cell use phenol as sole carbon source. Phenol, an aromatic hydrocarbon, is degraded by different microbes. *Pseudomonas putida* is the main organism for the degradation of phenol as the carbon source [26]. Fungi are familiar for their diversity and significant capacity to metabolize phenol compounds; a few fungal species namely *Trichosporoncutaneum, candida* species, *Rhodotorula*species were able to make use of phenol as their carbon and energy source *Fusarium flocciferum* Anselm and Novais (1984) whiterotfung i [27] *Phanerochaete chrysosporium* [28, 29] shown to degrade phenols. *Aspergillus chlorophenolicus* use monochlorophenols as their carbon source in aerobic batch culture has been analyzed.

5.1 Aerobic Biodegradation of Phenol

In early nineteenth century, aerobic biodegradation has been studied. *Acientobacter calcoceticus, Pseudomonas* species, and *Candida tropicalis* undergo phenol degradation by aerobic pathway and majority of the eukaryotes in general utilize orthopathway. There is widespread application in waste water treatment (Fig. 2).

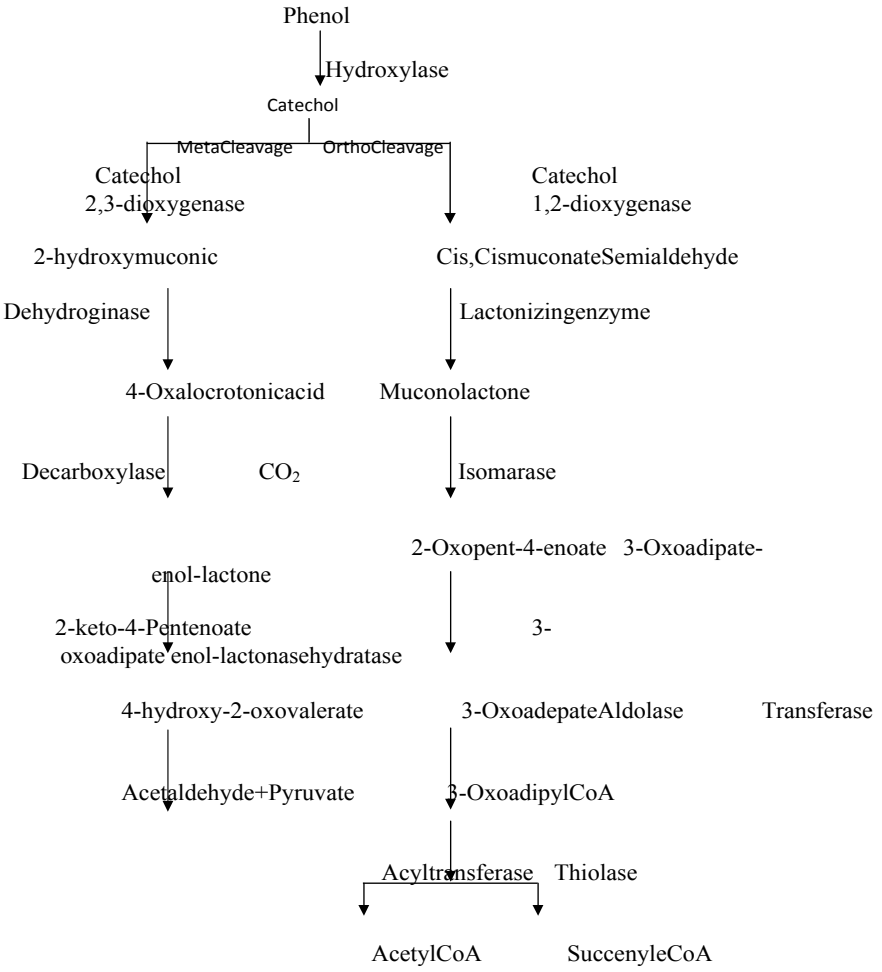

Fig. 2 Flow chart of aerobic degradation pathway for phenol

5.2 Anaerobic Biodegradation of Phenol

Phenol degraded in absence of oxygen and is not as much of superior to the aerobic process which is based on the similarity with the anaerobic benzoate pathway proposed for *Paracoccus denitrificans* in 1970 [30]. The organisms which biodegrade phenol in the absence of oxygen were *Thauera aromatic* and *Desulphobacterium phenolicum* (Fig. 3).

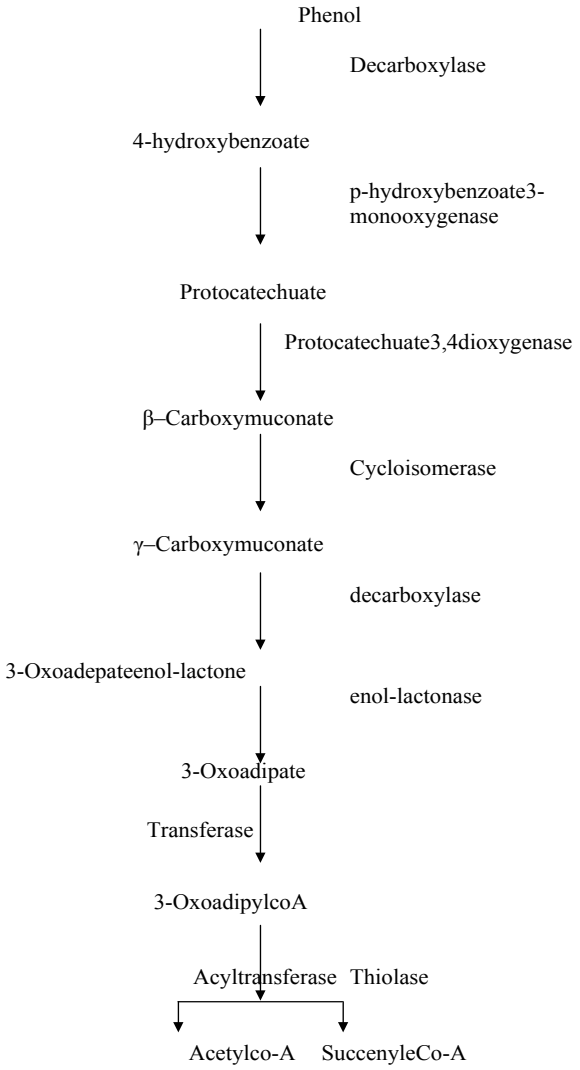

Fig. 3 Flowchart of anaerobic degradation pathway for phenol. *Source* Basha et al. [31]. @ Society of Applied Sciences

6 Fuel Cells

The chemical energy is changed into electrical energy designed in the simple principle of hydrogen fuel cells. The concept was revealed by German scientist Christian Friedrich Schonbein. MFC concept was initially introduced by Potter [32]. In early nineteenth century (1839) Welsh scientist and barrister Sir William Robert Grove fabricated the first fuel cell based on this concept [33, 34].

In 2006, Logan and Regan observed and produced biocurrent from live culture of *E. Coli* and *Saccharomyces* sp. Active biocatalysts are able to generate electrons via anabolism of organic and inorganic matters to anode electrode. Power production from axenic cultures of microbes such as Geobacter sulfurreducens generates electricity by direct oxidation of glucose [35], *C. butyricum* were Fe(III) reducing bacteria [36] and sulfide reducers can liberate bioelectricity. *Pseudomonas aeruginosa, Streptococcus lactis, Shewanellao neidensis, and R. ferrireducens* [37–39].

Three major components: an anode electrode, cathode electrode, and electrolyte (membrane) are present in the fuel cells. The water contains oxygen, hydrogen, and electrons; Hydrogen is used as energy in the cell, and after oxidizing in an anode electrode, positive H^+ ions and electrons are formed; then protons and electrons pass through the membrane and external circuit, respectively [40, 41]. Bioelectricities produced by microbial fuel cells in anaerobic anode chambers and carbohydrates are used as a substrate and liberate electrons. Some of the microbes are capable of generating bioelectricity from different types of substrate and reductive substances [42, 43].

New approaches to treat wastewater and generate bioelectricity have attracted a huge number of scientists. Habermann and Pommer [44] used MFCs to treat wastewater. The novel technology used the microorganisms which were actively catabolize and oxidized organic and inorganic substrate present in sewage water, electrons are liberated along with stable biocurrent is formed; it is safe, green, and eco-friendly approach for organic waste management [45].

7 Microbial Fuel Cells

All over the world energy need is ever increasing. In this view, fossil fuels have created to a major portion of the total energy requirement, in one way or another. In addition, the oxidization of fossil fuels generates a lot of carbon dioxide, which is a major greenhouse gas and has explained dangerous outcomes on the environment. It has consequently produced an enormous deficiency of fossil fuel sources and is causing an ecological imbalance. Therefore, the search for substitute sources of energy generation that are cheap and eco-friendly has become a superior requirement [46].

Microbial fuel cells (MFC) technology, which generates energy especially from oxidation of organics by the metabolic activity of microorganisms, seems to be attractive to warrant energy power generation [46, 47] (Rabaey et al. 2003). The use

of MFC as renewable energy source for power generation is considered as a reliable, clean, efficient process, which utilizes renewable methods are alternative tool most commonly used non sustainable sources and does not cause any toxic by-product. Therefore, in recent years, MFCs have shown to be a potent technology for recovery and in situ conversion of chemical energy into electrical energy [46]. Microbial fuel cell (MFC) technology, which make use of microbes to change the chemical energy of organic compounds into electricity, is considered a promising alternative. Broad studies have established new penetrations into MFC, which prove that a extensive collection of carbon sources including wastes can be occupied using a variety of microbes. Therefore, microbial metabolism of wastes using novel bioremediation approaches such as MFC for energy production is recognized as the effective and environmentally benign approach.

Microbial fuel cells (MFCs) hold great promise for sustainable wastewater treatment due to their low-cost and to maintain ecological balance [48]. In their simplest form, the traditional two chambers—MFCs typically have an anode and a cathode separated by a proton exchange membrane (PEM) to avoid the exodus of electrolytes from one chamber to the other [49]. When organic compounds are infused to the anode chamber, electrochemically active and bacteria oxidize the substrates with producing electrons and protons. Electrons are then transferred from anode to the cathode via an external circuit, while the protons diffuse through the PEM [50–52]. By serving as terminal electron acceptors in the cathode compartment, metals can be electrochemically reduced and eventually be recovered from the cathode surface [53].

Microorganisms utilize organic matter such as wastewater or combined nutrients to generate electrons, protons, and carbon dioxide on the anode. The electrons then pass through the electric meter to the cathode. At the cathode, microorganisms can turn the electrons to reduce oxygen to water in the presence of air or convert nitrate to nitrite or N_2 or convert CO_2 to acetate [54].

The method of MFCs is a type of bioelectrochemical process carried out by bacteria catalyze oxidation (adding of O_2 or removal of H_2) or reduction (adding of H_2 or removal of O_2) by oxido-reductases to generate electric current. MFCs system contains cathode and anode divided by cationic exchange membrane. The bacteria release electrons by utilizing organic compounds by substrate oxidation in the negative terminal of the anode chamber and are transmitted to the cathode compartment (positive terminal) through a conductive substance. Organic substrates were utilized and released electrons through enzymatic reactions carried out in the aerobic and anaerobic cycle of bacteria. The metabolic potential gain for bacteria is straightly related to the difference between anode potential and substrate redox potential. The MFC compartment plan is yet under research to improve its performance. The understanding of bacteria has increased the efficiency for the reaction [55].

7.1 The Mechanism of Electron Transfer Can Occur in Three Different Pathways Clark and Nanette [56]

1. First, the electrons can be transferred to the anode through a soluble mediator in the solution bathing the electrode.
2. Second, Electrons can be transferred directly to the anode through proteins found on the outer membrane of the bacteria. For example, microorganisms from *Geobacteraceae* family transfer electrons to electrodes using cytochromes on the outer membrane. *Shewanella oneidensis* also uses cytochrome C to transfer electrons but requires an anaerobic environment to convert lactate to acetate.
3. In some cases, Pili or Nanowire transmit the electrons to the anode. In contrast electrode—oxidizing organisms use electrons from the cathode to reduce substances in the cathode chamber. For example, G. sulfurreducens reduces fumarate to succinate with electrons obtained from cathode. Interestingly the susbtrates that these organism need for the redox reaction can be readily obtained from waste water or contaminated water which would provide energy and clean up the environment.

8 Microbial Fuel Cell in Wastewater Treatment

A microbial fuel cell (MFC) is a bioelectrochemical method that can transform chemical energy to electrical energy by microbial catalyst as an electrode. Pollutants in the wastewater, including carbon, nitrogen, phosphorus, or heavy metals, can be degraded/stabilized in the compartments of MFC [57–60]. Simultaneously, the chemical energy trapped in these compounds is converted into electricity (Fig. 6).

It has been revealed that MFC (Microbial fuel cell) can process wastewater immediately into direct electric current and advantageous substrates such as H, H, O, and CH. Wastewater treatment can enhance sustainable development at which point refiner and energy scavenging can be attained concurrently; some of these pollutants are pathogenic microorganisms, hydrocarbon, nitrogen, phosphorus, and heavy metals, endocrine disrupters and organic matter. This synthesis is converted into electricity from the trapped chemical energy.

MFC a variant of bioelectrochemical system is an emerging technology, where bioenergy is produced through oxidation of organic matter by microorganisms—acting as biocatalyst. Several wastewater treatment techniques are chemical treatment, aerobic treatment, anaerobic digestion, and membrane filtration. MFCS have their own distinctive characteristic such as immersive hydropower, reduced socioeconomic activities, operating balance of high quality and recessive economic organization (Fig. 4). In contrast to aerobic septic system, MFCs provide less sludge and decrease energy depletion. It's also good for anaerobic digestion technology on account of its operational tolerance in drastic situations, like low temperatures

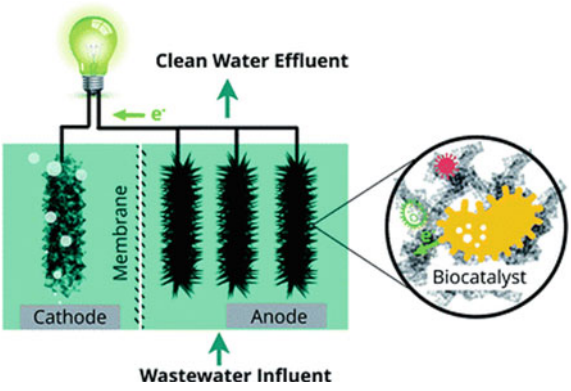

Fig. 4 Schematic of using MFCs for simultaneous wastewater treatment and energy recovery. *Source* Guo et al. [61]. @The Royal Society of Chemistry 2020

(20 °C) and low substrate centralization. Nevertheless, MFCs has its own flaws like short life span, low manufacturing rates, finite planning, unreliability, and disruption in the maintenance of microbe-based systems and also suffer from membrane fouling (Fig. 6).

MFC exhibited in 2001 the relation between electricity production and wastewater treatment, from domestic wastewater, while at the same time accomplishing biological wastewater treatment for the electricity generation. For several years, researchers have been developing incredible progress on structural design and electrode material enhancement to magnify MFC action. Following this, MFCs were extensively used to eliminate several contaminants in wastewater. The methodical data on MFC biocatalysts is still missing in terms of its significance in concurrent refiner removal and energy production. This analysis focuses to fill up the highlight main future research areas to additionally progress their accomplishment.

The first practical devices to be powered by MFC technology was reported in 2008 [62]. Microbial fuel cells (MFCs) have been reported to treat a wide range of wastewater and are capable of converting the energy contained in wastewater directly into electricity and useful chemicals like H_2, H_2O_2, CH_4, etc. (Tang et al. 2015) [63]. Compared to aerobic treatment, MFCs produce less sludge and reduce energy consumption. It is also superior to anaerobic digestion technology owing to its operation flexibility in relatively extreme conditions, like low temperatures.

MFCs gain a competitive advantage over other water treatment technologies due to their unique features such as huge energy benefits, less environmental impact, good operating stability, and high economic efficiency [64] (Fig. 5). Compared to aerobic treatment MFCs produces less sludge and reduce energy consumption. It is also superior to anaerobic digestion technology owing to its operation flexibility in relatively extreme condition, like low temperature and low substrate concentration.

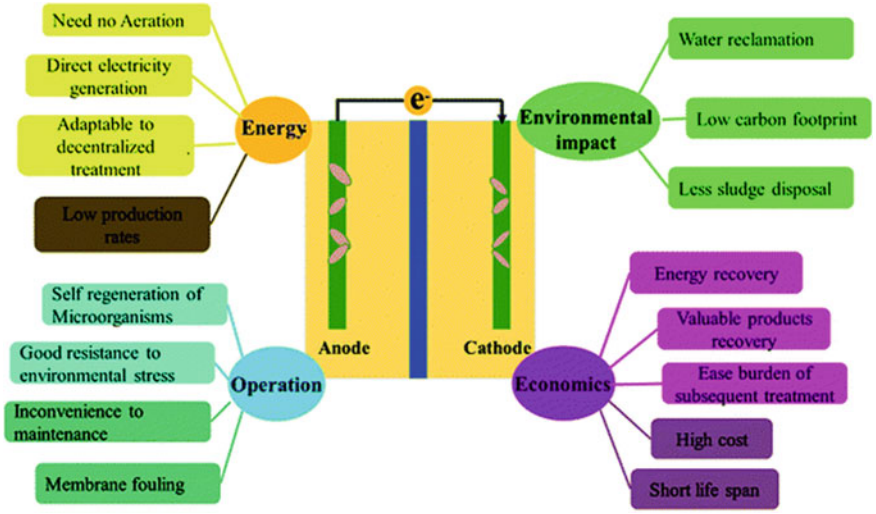

Fig. 5 Advantages and disadvantages of MFC technology for treating wastewater. *Source* Guo et al. [61]. @The Royal Society of Chemistry 2020

9 Biocatalyst Action Mechanisms in MFCs

Several diverse biocatalystic degradation of pollutants and produce electric current in MFCs. It has various allocations and capacities in various MFCs arrangements. In the MFC organization, there is interspecific coordination among chemical element-degenerating bacteria, electrogenic bacteria, and additional out-numbered bacteria.

Initially, the pollutant-degenerating bacteria in the microbial electrode-electron transfer upgraded the initial modification of chemical elements. It helped along electroactive bacteria and further microbes degenerate the biodegradable circle decomposition products enabling inter-species permitting association. This could elucidate the magnified removal effectiveness and control engendering execution in MFCs. Each category plays a particular role in a culturally diverse population, to set up cooperation in pollutants degradation, electricity generation, and the protection of the community against injurious ecological conditions.

10 Conclusion

MFC is a state-of-the-art technology for electricity generation from metabolism of microorganisms. In this chapter, we have dealt with phenolic compounds exist in waterbodies due to discharge of polluted wastewater from industrial, agricultural, and domestic activities into waterbodies. Some of them such as phenols and phenolic compounds are very hazard to the environment and leads to cause death of microbes.

In MFC, they are used for electric-power generation and also they are transformed into less toxic metabolites, which demonstrates its another potential use in waste management and pollution control. Presently, a large number of microbes and a waste variety of substrates (including phenol and phenolic compound) have been used to produce electricity. However, a major drawback of this method is that the power output is very low and scaling up leads to a decrease in power output. This is the main reason why this practical purpose has yet not been commercialized therefore, a lot more work is required so that this technology becomes efficient, applicable, and widely accepted.

References

1. Tauseef SM, Abbasi T, Abbasi SA (2013) Energy recovery from wastewaters with high-rate anaerobic digesters. Renew Sustain Energy Rev 19:704–741. https://doi.org/10.1016/j.rser.2012.11.056
2. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manag 92(3):407–418
3. Wang H, Ren ZJ (2014) Bioelectrochemical metal recovery from wastewater: a review. Water Res 66:219–232
4. Leceta I, Guerrero P, De La Caba K (2013) Functional properties of chitosan-based films. Carbohyd Polym 93(1):339–346
5. Martillanes S, Rocha-Pimienta J, Cabrera-Bañegil M, Martín-Vertedor D, Delgado-Adámez J (2017) Application of phenolic compounds for food preservation: Food additive and active packaging. In: Phenolic compounds—Biological activity. IntechOpen, London, UK, pp 39–58
6. Raza W, Lee J, Raza N, Luo Y, Kim KH, Yang J (2019) Removal of phenolic compounds from industrial waste water based on membrane-based technologies. J Ind Eng Chem 71:1–18
7. Temoçin Z, Kutluer S (2020) Conversion of phenolic compound in aqueous solution using immobilized peroxidase onto blend nanofiber. In: EurAsia waste management symposium. Istanbul/Türkiye. http://www.eurasiasymposium.com/EWMS/files/Poster/175_Kutluer-22.pdf
8. Busca G, Berardinelli S, Resini C, Arrighi L (2008) Technologies for the removal of phenol from fluid streams: a short review of recent developments. J Hazard Mater 160(2–3):265–288
9. Michałowicz J, Duda W (2007) Phenols—Sources and toxicity. Polish J Environ Stud 16(3)
10. Mu'Azu ND, Jarrah N, Zubair M, Alagha O (2017) Removal of phenolic compounds from water using sewage sludge-based activated carbon adsorption: a review. Int J Environ Res Public Health 14(10):1094
11. Harborne JB (1964) Biochemistry of phenolic compounds. Academic Press, London, UK
12. Lattanzio V (2013) Phenolic compounds: introduction. Nat Prod 50:1543–1580
13. Raza W, Lee J, Raza N, Luo Y, Kim KH, Yang J (2019) Removal of phenolic compounds from industrial waste water based on membrane-agency; Toxic Substances and Disease Registry (ATSDR) (2006) Toxicological Profile for Phenol, U.S. Department Of Health And Human Services, Public Health Service
14. International Agency for Research on Cancer (IARC) (1989) Phenol. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, vol 47. World Health Organization, pp 263–287
15. Kazemi P, Peydayesh M, Bandegi A, Mohammadi T, Bakhtiari O (2014) Stability and extraction study of phenolic wastewater treatment by supported liquid membrane using tributyl phosphate and sesame oil as liquid membrane. Chem Eng Res Des 92(2):375–383
16. Chakraborty S, Bhattacharya T, Patel TN, Tiwari KK (2010) Biodegradation of phenol by native microorganisms isolated from coke processing wastewater. J Environ Biol 31(3):293

17. Park J, Brown MT, Depuydt S, Kim JK, Won DS, Han T (2017) Comparing the acute sensitivity of growth and photosynthetic endpoints in three Lemna species exposed to four herbicides. Environ Pollut 220:818–827
18. Jin X, Gao J, Zha J, Xu Y, Wang Z, Giesy JP, Richardson KL (2012) A tiered ecological risk assessment of three chlorophenols in Chinese surface waters. Environ Sci Pollut Res 19(5):1544–1554
19. Ceylan Z, Şişman T, Yazıcı Z, Altıkat AÖ (2016) Embryotoxicity of nitrophenols to the early life stages of zebrafish (Daniorerio). Toxicol Ind Health 32(8):1414–1422
20. Chen R, Yuan L, Zha J, Wang Z (2017) Developmental toxicity and thyroid hormone-disrupting effects of 2,4-dichloro-6-nitrophenol in Chinese rare minnow (Gobiocyprisrarus). Aquat Toxicol 185:40–47
21. Ge T, Han J, Qi Y, Gu X, Ma L, Zhang C et al (2017) The toxic effects of chlorophenols and associated mechanisms in fish. Aquat Toxicol 184:78–93
22. Musa ZJ, Bandela N (2014) Estimation of hazardous phenolic compounds in industrial wastewater. Eur Acad Res II (8):10999–11006
23. Saha NC, Bhunia F, Kaviraj A (1999) Toxicity of phenol to fish and aquatic ecosystems. Bull Environ Contam Toxicol 63(2):195–202
24. Hussain A, Dubey SK, Kumar V (2015) Kinetic study for aerobic treatment of phenolic wastewater. Water Resour Ind 11:81–90
25. Ramírez EE, Asunción MD, Rivalcoba VS, Hernández AL, Santos CV (2017) Removal of phenolic compounds from water by adsorption and photocatalysis. https://www.intechopen.com/chapters/53679. https://doi.org/10.5772/66895
26. Anselmo AM, Novais JM (1984) Isolation and selection of phenol-degrading microorganisms from an industrial effluent. Biotech Lett 6(9):601–606
27. Valli K, Gold MH (1991) Degradation of 2,4-dichlorophenol by the lignin-degrading fungus Phanerochaete chrysosporium. J Bacteriol 173(1):345–352
28. Kennes C, Lema JM (1994) Simultaneous biodegradation of p-cresol and phenol by the basidiomycetePhanerochaetechrysosporium. J Ind Microbiol 13(5):311–314
29. Yong L, Yan L, Wang Y, Zhou S, Jiajun F, Zhang J (2009) Biodegradation of phenolic compounds from coking waste water by immobilized white rot fungus *Phanerochaete chrysosporium*. J Hazard Mater 165(1–3):1091–1097
30. Raza W, Lee J, Raza N, Luo Y, Kim K-H, Yang J, Williams RJ, Evans WC (1975) The meta bolism of Benzoate by *Moraxella* sp. Through an aerobic nitrate respiration. Biochem J 148:1–10
31. Basha KM, Rajendran A, Thangavelu V (2010) Recent advances in the biodegradation of phenol: a review. Asian J Exp Biol Sci 1(2):219–234
32. Potter MC (1911) Electrical effects accompanying the decomposition of organic compounds. Proc R Soc London. Ser B, Contain Pap Biol Charact 84(571):260–276
33. Grote M (2010) Surfaces of action: cells and membranes in electrochemistry and the life sciences. Stud Hist Philos Sci Part C: Stud Hist Philos Biol Biomed Sci 41(3):183–193
34. Guo Q, Furukawa K, Sopher BL, Pham DG, Xie J, Robinson N et al (1996) Alzheimer's PS-1 mutation perturbs calcium homeostasis and sensitizes PC12 cells to death induced by amyloid β-peptide. Neuroreport 8(1):379–383
35. Chaudhuri SK, Lovley DR (2003) Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat Biotechnol 21(10):1229–1232
36. Park HS, Kim BH, Kim HS, Kim HJ, Kim GT, Kim M et al (2001) A novel electrochemically active and Fe (III)-reducing bacterium phylogenetically related to Clostridium butyricum isolated from a microbial fuel cell. Anaerobe 7(6):297–306
37. Ringeisen BR, Henderson E, Wu PK, Pietron J, Ray R, Little B et al (2006) High power density from a miniature microbial fuel cell using Shewanella oneidensis DSP10. Environ Sci Technol 40(8):2629–2634
38. Ringeisen BR, Ray R, Little B (2007) A miniature microbial fuel cell operating with an aerobic anode chamber. J Power Sour 165(2):591–597

39. Vega CA, Fernández I (1987) Mediating effect of ferric chelate compounds in microbial fuel cells with Lactobacillus plantarum, Streptococcus lactis, and Erwiniadissolvens. Bioelectrochem Bioenergy 17(2):217–222
40. Rahimnejad M, Mostafa G, Ghasem N, Ghoreyshi A, Bakeri G, Nejad SH, Talebnia F (2012) Acetone removal and bioelectricity generation in dual chamber microbial fuel cell. Am J Biochem Biotechnol 8(4):304–310
41. Steele BC, Heinzel A (2001) Materials for fuel-cell technologies. Nature 414(6861):345–352
42. Larminie J, Dicks A, McDonald MS (2003) Fuel cell systems explained, vol 2. Wiley, Chichester, UK, pp 207–225
43. Norbeck JM, Heffel JW, Durbin TD, Tabbara B, Bowden JM, Montano MC (1996) Hydrogen fuel for surface transportation, vol 160
44. Habermann W, Pommer EH (1991) Biological fuel cells with sulphide storage capacity. Appl Microbiol Biotechnol 35(1):128–133
45. Najafpour G (2015) Biochemical engineering and biotechnology. Elsevier
46. Logan BE (2004) Biologically extracting energy from wastewater: biohydrogen production and microbial fuel cells. Environ Sci Technol 38(9):160–167
47. Mohan SV, Saravanan R, Raghavulu SV, Mohanakrishna G, Sarma PN (2008) Bioelectricity production from wastewater treatment in dual chambered microbial fuel cell (MFC) using selectively enriched mixed microflora: effect of catholyte. Biores Technol 99(3):596–603
48. Chouler J, Padgett GA, Cameron PJ, Preuss K, Titirici MM, Ieropoulos I, Di Lorenzo M (2016) Towards effective small scale microbial fuel cells for energy generation from urine. Electrochimicaacta 192:89–98
49. Ho NAD, Babel S, Sombatmankhong K (2018) Bio-electrochemical system for recovery of silver coupled with power generation and wastewater treatment from silver (I) diammine complex. J Water Process Eng 23:186–194
50. Mathuriya AS, Yakhmi JV (2014) Microbial fuel cells to recover heavy metals. Environ Chem Lett 12:483–494
51. Miskan M, Ismail M, Ghasemi M, Jahim JM, Nordin D, Bakar MHA (2016) Characterization of membrane biofouling and its effect on the performance of microbial fuel cell. Int J Hydrog Energy 41(1):543–552
52. Nimje VR, Chen CC, Chen HR, Chen CY, Tseng MJ, Cheng KC et al (2012) A single-chamber microbial fuel cell without an air cathode. Int J Mol Sci 13(3):3933–3948
53. Ucar D, Zhang Y, Angelidaki I (2017) An overview of electron acceptors in microbial fuel cells. Front Microbiol 8:643
54. Dolch K, Danzer J, Kabbeck T, Bierer B, Erben J, Förster AH et al (2014) Characterization of microbial current production as a function of microbe-electrode-interaction. Bioresour Technol 157:284–292
55. Ramírez-Vargas CA, Prado A, Arias CA, Carvalho PN, Esteve-Núñez A, Brix H (2018) Microbial electrochemical technologies for wastewater treatment: principles and evolution from microbial fuel cells to bioelectrochemical-based constructed wetlands. Water 10(9):1128
56. Clark DP, Pazdernik NJ (2016) Chapter 12—Environmental biotechnology. In: Clark DP, Pazdernik NJ (eds) Biotechnology, 2nd edn. Academic Cell, pp 393–418
57. Heijne AT, Liu F, Weijden RVD, Weijma J, Buisman CJ, Hamelers HV (2010) Copper recovery combined with electricity production in a microbial fuel cell. Environ Sci Technol 44(11):4376–4381
58. Nitisoravut R, Regmi R (2017) Plant microbial fuel cells: a promising biosystems engineering. Renew Sustain Energy Rev 76:81–89
59. Tao Q, Zhou S (2014) Effect of static magnetic field on electricity production and wastewater treatment in microbial fuel cells. Appl Microbiol Biotechnol 98(23):9879–9887
60. Zhao LX, Kong FY, Wang X, Wen Q, Sssun Q, Wu Y (2009) Cr(VI)-containing wastewater treatment coupled with electricity generation using microbial fuel cell. Modern ChemInd 29:37–39
61. Guo Y, Wang J, Shinde S, Wang X, Li Y, Dai Y, Ren J, Zhang P, Liu X (2020) Simultaneous wastewater treatment and energy harvesting in microbial fuel cells: an update on the biocatalysts. RSC Adv (Rev Article) 10: 25874–25887. https://doi.org/10.1039/D0RA05234E

62. Tender LM, Gray SA, Groveman E, Lowy DA, Kauffman P, Melhado et al (2008) The first demonstration of a microbial fuel cell as a viable power supply: powering a meteorological buoy. J Power Sour 179(2):571–575
63. Xu X, Zhao Q, Wu M, Ding J, Zhang W (2017) Biodegradation of organic matter and anodic microbial communities analysis in sediment microbial fuel cells with/without Fe(III) oxide addition. Biores Technol 225:402–408
64. Li F, Chen L, Knowles GP, MacFarlane DR, Zhang J (2017) Hierarchical mesoporous SnO_2 nanosheets on carbon cloth: a robust and flexible electrocatalyst for CO_2 reduction with high efficiency and selectivity. Angew Chem 129(2):520–524

Removal of Toxic Metal Ions from Wastewater Through Microbial Fuel Cells

Asim Ali Yaqoob, Mustapha Omenesa Idris, Akil Ahmad, Najwa Najihah Mohamad Daud, and Mohamad Nasir Mohamad Ibrahim

Abstract Water pollution is rising through contaminated substances that are a source of serious hazardous alarm to living organisms. Due to increasing population density, factories, industries, loss of water reserves, inappropriate disposal of agro-waste and local daily wastes and other factors, a wide range of contaminants are entering the natural ecosystem. In Malaysia, around 99% of people are using surface water for their life survival due to the presence of different toxic pollutants in water. Few states of Malaysia used ground water for different purposes, i.e. only 1%. Groundwater body pollution is a serious issue for the whole wide at present time. Toxic metals, organic pollutants dyes, etc., are major causes to distribute the aquatic life. Recently, modern research invented a design called microbial fuel cells to remove pollutants from wastewater. Microbial fuel cells (MFCs) are still an emerging topic because MFCs can generate energy along with wastewater treatment at a low cost. In this chapter, removal of toxic metals through MFC and its applications was discussed to explore the research gap. Despite many developments in MFCs, it still needs more effort to make low-cost techniques by improving their parameters. The present chapter also describes some future perspectives regarding MFCs' working performance in a practical sense. Reported literature data also revealed that future research

A. A. Yaqoob · M. O. Idris · N. N. M. Daud · M. N. M. Ibrahim (✉)
School of Chemical Science, Universiti Sains Malaysia, 11800 Penang, Malaysia
e-mail: mnm@usm.my

M. O. Idris
e-mail: idris.mo@student.usm.my

A. A. Yaqoob
Research Institute for Advanced Industrial Technology, College of Science and Technology, Korea University, Sejong 30019, South Korea

M. O. Idris
Department of Pure and Industrial Chemistry, Kogi State University, P.M.B, Anyigba 1008, Kogi State, Nigeria

A. Ahmad
Chemistry Department, College of Sciences and Humanities, Prince Sattam Bin Abdulaziz University, Al-Kharj, Saudi Arabia

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_15

must be on environment hazard assessment and aquatic life which is due to the presence of pollutants in drinking water.

Keywords Microbial fuel cells · Toxic metals · Dyes · Wastewater remediation · Organic pollutant · MFC applications

1 Introduction

Environmental water pollution is growing in the modern era through toxic substances that cause hazardous alarm to human beings. The high rate of industrialization, humanity, natural resources degradation, high agriculture household waste, etc., is causing a wide array of toxins in the natural environment [1, 2]. Malaysian approximately 99% use surface water, while they use only 1% groundwater for a variety of residential uses. Malaysia has nearly 580 km^3 of total water resources annually. By and large, today in Malaysia, purified surface water is commonly utilized as a major source of drinking water, however, in few states of the country like Perlis, Kelantan, Sabah, Kedah, Pahang, Terengganu, Pulau Pinang and Sarawak are major consumers of groundwater for drinking [3]. Among all problems, toxic heavy metals are major problems for aquatic life [4, 5]. These pollutants have a very bad impact on human health, and they are very dangerous for water resources. Water is a major component for all living organisms [6]. Heavy metals are primarily concerned with metallic elements that have a high level of toxicity and density effect even at low concentrations. It is generally a collective character which refers to metalloids and metal elements with high density, even more than water. Heavy metal in the water poses a significant hazard to living organisms. [7, 8]. Metal finishing, electroplating, chemical processing industries and dyeing all create it. It is non-biodegradable, has a high density and is soluble in both surface and ground water [9, 10]. If ingested in excess of the permitted concentration, it can become a major cause of serious health concerns for humans. Contamination of water is caused by a variety of reasons. Various human activities such as industrial operations, agriculture, mining and many other activities have made ground and surface water supplies vulnerable [11–13]. Due to poor waste disposal and wastewater management, these activities are to blame for increasing heavy metal concentrations in water sources. Heavy metal may also enter the body through food, water and the air we breathe. Arsenic (As), mercury (Hg), cadmium (Cd), manganese (Mn), silver (Ag), copper (Cu), lead (Pb), zinc (Zn), chromium (Cr), thallium (Tl), nickel (Ni) and iron (Fe), are the most often detected metals in Malaysian wastewater [14]. When a large quantity of toxic metal finds its way into the human body, it can create significant health problems. For example, chromium can affect irritations in the skin, nerve tissue, ulceration and serious damage to the kidneys, circulatory structure and liver [15]. Lung illness, renal failure and bone abnormalities can all be caused by excessive cadmium exposure. Ni and Cu, on the other hand, can cause a variety of illnesses, including renal failure, liver issues, anaemia, intestinal inflammation, stomach discomfort and blood

circulatory disease. Similarly, Pb and Hg are the most hazardous to human health; they can induce Huter Russel, acrodynia, syndrome and Minamata disease, and also harm the respiratory system, brain, skin kidneys and heart [16–18]. Although arsenic is not an essentially metal, its characteristics are intermediate between non-metals and metals, making it a semi-metal. If arsenic levels in the body are high enough, it can cause significant health problems. The most common source of the poison arsenic is ground natural water, which has high amounts of toxin. The scientific community investigated a case in 2007 and discovered that virtually 137 million humans are harmed by drinking arsenic-based wastewater [19]. To overcome the heavy metal and organic dyes pollutants in drinking water, there are many reported methods are used for waste water treatment such as ozonation, in situ and ex situ treatment, electrochemical degradation, washing, coagulation, electrolytic reduction, ion-exchange adsorption, monitoring natural recovery, thermal treatment, photocatalysis, adsorbent, biochemical stabilization and chemical precipitation [20–23]. They all produced superior results, but there were some big downsides, such as the high energy required to run these systems, the high chemical consumption, the heavy waste products produced, and the fact that they are all expensive. To run these all traditional methods at a commercial level, the researcher requires a significant maintenance expense. So, in 1976, Suzuki et al. established a new technology known as the microbial fuel cells (MFCs), however, this notion was previously presented by M. C. Potter in 1911, who proposed that microorganisms be used to generate energy. Later, in 2007, a researcher group from the University of Queensland in Australia modified MFCs to make them fully functional in order to create energy while also treating water. Heavy metals and organic contaminants were degraded/removed from water using microorganisms [24–26]. This method received a lot more attention than other traditional ways. MFCs are devices in which microorganisms break down organic contaminants and harmful metals via redox reaction in wastewater to generate an electron flow known as electricity. MFCs are an innovative, environmentally beneficial and low-cost way of generating energy in the water treatment process [27, 28]. Anode and cathode chambers are the two main components of MFCs. In the presence of an oxidative environment, exoelectrogenic bacteria transmit electron to anode electrode and subsequently electron to cathode chamber through external circuit, whereas proton goes straight from anode to cathode [29, 30]. A systematic presentation was presented in Fig. 1. However, carbon substrate, concentration of ion, internal resistance, electrode spacing, biocatalyst, MFCs configuration and electrode material characteristics are only a few of the numerous elements that influence MFCs performance [31]. The electrode material is a critical component in making MFCs more dependable and prolific on a large scale. Electrotrophic microorganisms in MFCs take electrons from electrodes and transform a hazardous chemical into something less poisonous [32]. Many exoelectrogens in MFCs can transfer electrons from electrodes via four mechanisms: short-range electron transfer via redox-active proteins, soluble electron shuttling molecules and long-range electron transport via conductive pili, as well as direct interspecies electron transfer. A pili-typed bacterial species have metal-like conductivity, long-range electron transport via conductive pili is the most common method [33]. Carbonaceous electrode materials (such as the

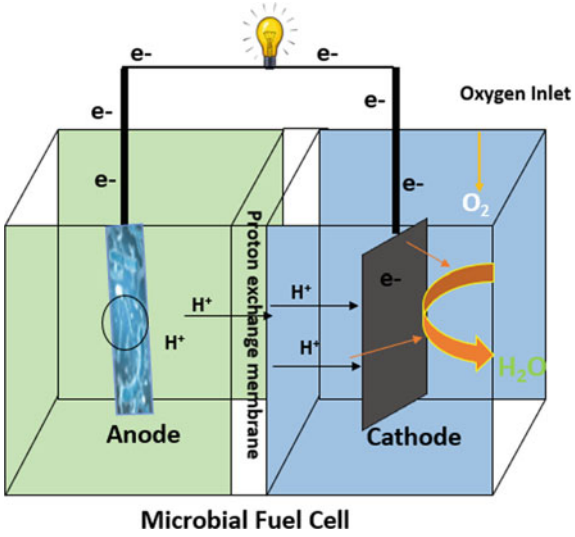

Fig. 1 Systematic diagram of MFCs model. Reproduced from Ref. [39] with Elsevier permission

graphite plates, carbon black, carbon cloth, carbon fibre, carbon brush, carbon mesh, carbon papers and so on), metal–metal oxide electrodes (Zn, Ag, Cu, Au, Pt, ZnO, TiO_2, etc.) and conductive polymers have all been reported to work as electrodes in MFCs [27, 34]. Excellent electrical conductivity, great stability to chemicals, strong thermal and mechanical stability, large surface area, low resistance and great biocompatibility are all characteristics of a good electrode material. During our literature survey, it was found that graphene oxide along with derivatives are the most effective and suggestive materials for electrodes [35]. Due to its enormous surface area, outstanding mechanical and thermal durability, strong conductivity and other properties, graphene oxide is becoming a more popular material. Because it has a theoretical surface area of 2630 m^2/g, graphene oxide can decrease the cost issue in MFCs while also providing good results in power production and water treatment. The traditional material surface area ranges from 90 to 200 m^2/g [29]. The conductivity of conducting polymers and other materials composites is very impressive [36]. However, it is recommended that the scientific community focus on developing conducting polymer composites with highly conductive metals in order to improve the effectiveness of the MFCs electrode and address a variety of other issues [37]. This chapter attempts to describe the importance of a new novel technique, MFCs, and how it works to degrade/remove heavy metal from drinking water [38]. The electrode is a major component of MFCs and applications of MFCs with their future perspectives were also assessed in this chapter. The article elaborated on different electrode materials' efficiency regarding the removal of pollutants (heavy metals). The literature review data shows that future research on human health and environment hazard assessment, which is due to excess of heavy metal and organic pollutants

in ground and surface water, is an emerging topic for the scientific community, especially for Malaysian researchers. There is a crucial need to understand and explore the risks of organic pollutants and toxic metals in drinking water.

2 Removal Mechanism of Metals Through Microbial Fuel Cells

To date, a variety of physical, chemical, biological and analytical methods for heavy metal remediation have been proposed. MFCs are the most practical, cost-efficient and environmentally beneficial solution for removing heavy metals while also producing electricity. In the remediation of heavy metals in MFCs, biological processes are extremely important. Electrotrophs are microorganisms with the ability to receive electron charges from electrodes, either the anode or cathode [40, 41]. This fact points to a new path for heavy metal reduction treatment. They get rid of the heavy metals from the microorganisms via a reduction process at the cathode electrode, while carbon source substrates are oxidized at the anode and aid to donate electrons [42]. Many kinds of bacteria have the ability to acquire electrons straight from electrodes. Many recent investigations have found that Geobacter species can directly absorb electron charges from electrodes. Many hazardous heavy metals, such as Hg, Ni, Cu, Hg, Zn, Pb, V and many others, are reduced by microbes using similar processes, e.g. G. sulfurreducens absorbs electrons straight from electrodes and reduces U(VI)–U(IV) form (soluble to insoluble). The U(IV) is a non-soluble substance that is adsorbed on the electrodes [42].

Watts et al. [43] investigated *G. sulfurreducens*, which has the capacity to reduce Cr(VI)–Cr(III), converting chromium's extremely hazardous oxidation state to a less toxic one. The anode electrode oxidizes the substrate (acetate) giving rise to electron discharges to microorganisms, while the cathode reduces the chromium. The reduction reaction is expressed as follows:

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Hao et al. [44] investigated vanadium removal using microbes such as *Enterobacter, Macellibacteroides* and *Lactococcus*. They found that the removal of vanadium had a 93.6% effectiveness with a large value current density of 543.4 mW/m^2. MFCs, on the other hand, can decrease the most dangerous heavy metal mercury. The redox potential of Hg^{2+} is -320 mV, making it an electron acceptor. In the presence of chloride (Cl^-) ions, the removal mechanism of Hg^{2+} in precipitate form occurs and the reduction by electrons happens at the cathode electrode, as illustrated below:

$$2Hg^{2+} + 2Cl^- \rightarrow Hg_2Cl_2(s)$$

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-$$

The end product, Hg_2Cl_2, is deposited at the cathode's bottom, whereas elemental Hg is deposited on the cathode's surface. The greatest power density attained during this procedure was 433.1 mW/m^2 [45]. Similarly, recently, some researchers described the reduction mechanism of different metals via MFCs configurations [46–48]. Some prominent reduction biochemical reactions are given below:

1. Conversion of Cd^{2+} into $Cd_{(s)}$

$$Cd^{2+} + 2e^- \rightarrow Cd_{(s)}$$

$$2Cd^{2+} + 2H_2O \rightarrow 2CdO + 4H^+$$

$$CdO + 2e^- + 2H^+ \rightarrow Cd_{(s)} + H_2O$$

2. Conversion of Pb^{2+} into $Pb_{(s)}$

$$Pb^{2+} + 2e^- \rightarrow Pb_{(s)}$$

$$2Pb^{2+} + 2H_2O \rightarrow 2PbO + 4H^+$$

$$PbO + 2e^- + 2H^+ \rightarrow Pb_{(s)} + H_2O$$

3. Conversion of Cr^{3+} into $Cr_{(s)}$

$$Cr^{3+} + 3e^- \rightarrow Cr_{(s)}$$

$$2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 6H^+$$

$$Cr_2O_3 + 6e^- + 6H^+ \rightarrow 2Cr_{(s)} + 3H_2O$$

4. Conversion of Ni^{2+} into $Ni_{(s)}$

$$Ni^{2+} + 2e^- \rightarrow Ni_{(s)}$$

$$2Ni^{2+} + 2H_2O \rightarrow 2NiO + 4H^+$$

$$NiO + 2e^- + 2H^+ \rightarrow Ni_{(s)} + H_2O$$

5. Conversion of Co^{2+} into $Co_{(s)}$

$$Co^{2+} + 2e^- \rightarrow Co_{(s)}$$

$$2Co^{2+} + 2H_2O \rightarrow 2CoO + 4H^+$$

$$CoO + 2e^- + 2H^+ \rightarrow Co_{(s)} + H_2O$$

6. Conversion of Ag^{1+} into $Ag_{(s)}$

$$Ag^{1+} + e^- \rightarrow Ag_{(s)}$$

$$2Ag^{1+} + 2H_2O \rightarrow Ag_2O + 4H^+$$

$$Ag_2O + e^- + 2H^+ \rightarrow Ag_{(s)} + H_2O$$

7. Conversion of Cu^{2+} into $Cu_{(s)}$

$$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$$

$$2Cu^{2+} + 2H_2O \rightarrow Cu_2O + 4H^+$$

$$Cu_2O + 2e^- + 2H^+ \rightarrow Cu_{(s)} + H_2O$$

For example, as a result, two main products may develop due to the Cu^{2+} reduction process in the MFCs: Cu_2O or $Cu_{(s)}$, whereas the electrons are released from the anode compartment's oxidation reactions of organic substrate [49]. MFCs convert the metal ions into the sludge form which can easily be recoverable in the form of oxides. During literature survey, it was found that no suitable chemical mechanism exists to explain how bacteria absorb electrons directly from the electrodes. This is a promising research focus for future studies. However, because the operation mechanism of MFCs is indirectly dependent on the efficiency of the anode, the anode has attracted substantial attention in the MFCs study. As a result, improving the anodic section of these systems takes precedence over all others.

3 Literature Survey of Pollutant Removal Through Microbial Fuel Cells

Water pollution is a big challenge for the modern world and there is a crucial need to overcome this problem. In the early era, the scientific community introduced many methods for water treatment, but they all carried out some major drawbacks [50]. The idea was to use the waste material to design MFCs and remove different types of pollutants from drinking water with the help of different microbes. MFCs still need

more attention because this method is still in the developing stages. This method is offering countless advantages to the scientific community to serve human being. It helps to remove the inorganic pollutants (metals, etc.) and are very potential regarding the reduction of heavy metals from higher toxic state to lesser toxic state to make water appropriate for drinking purpose [51]. MFCs are also offering sustainable energy sources along with water treatment by using waste material. However, nowadays the scientific community is giving a lot of attention to this method because it is an eco-friendly, low-cost method and carries the ability to use biodegradable material as fuel. MFCs have some components that are very useful and remarkable regarding pollutant removal such as electrodes, MFCs design. type of microbes [52, 53]. A suitable MFCs systematic design can provide enough space for electrodes to grow bacteria on the surface more effectively to enhance their working efficiency. The heavy metal does not biodegradable into toxic products. Therefore, high redox potential heavy metals can use electron acceptors to reduce and precipitate the metals [54]. MFCs are used to treat heavy metals but there were three reported processes for the generation of electrons, their movement and consumption, i.e. electrochemical, chemical-based reactions and bioelectrochemical. The biochemical reaction is the first step which carries out anode and helps to generate electrons during the metabolism process. The electrochemical phase takes over when an electron reaches the cathode by using an external path. It is considered the reduction of oxygen to convert into H_2O or hydrogen peroxide form. It can consider direct reductions of heavy metals [55, 56]. For example, a bacterial species *Geobacter sulfurreducens* got electrons from the surface of electrodes to reduce the U(VI) into U(IV) form. The insoluble state of U(IV) is adsorbed on electrodes. *G. sulfurreducens* had the ability to reduce any toxic, soluble state of Cr(VI) to insoluble Cr(III). Cr(VI) reduction is due to the oxidation of substrates (like glucose, acetate, etc.) at anode to give electrons to *G. sulfurreducens* (bacteria) and reduction process occurred at cathode [57].

3.1 Removal of Metal Ions

Heavy hazardous metals are found in wastewater from industries, hospitals and domestic sources. The toxic metals, on the other hand, pose several threats to human health and the environs due to their non-biodegradable nature, poisonous nature and their accumulation in the biosphere [58]. There are numerous traditional techniques for removing heavy metals from wastewater, such as physical, biological and chemical approaches, but they use a lot of energy, are difficult to operate and are thus unsuccessful. Another issue with traditional approaches is that when metal concentrations are between 1 and 100 mg/L, all methods become ineffective since the method efficiency is reduced [59]. Recently, MFCs have become an emerging study path for environment researchers and received increasing attention from a scientific community. MFCs have played an important part in waste water treatment and particularly in heavy metal degradation/recovery, such as copper, mercury, chromium, zinc, nickel and cadmium [60]. MFCs are bio-electrochemical cell types that are

regarded by employing various biocatalytic (metabolic) activities of the microorganisms to transform organic energy into electrical form. The reduction to the less polluted and insoluble form of less potential electrodes in soluble, very poisonous, metals like Cr(VI), Pb(II), Hg(II) Cd(II), etc. Many electric-generating bacteria have been described that are capable of reducing hazardous metals. However, no reduction process is possible to remove all heavy metals; certain require an oxidation stage for the metals in wastewater to be degraded. For instance, Arsenic is difficult to be degraded by decrease, oxidization at a precipitate formation anode electrode was necessary. Early on, MFCs working efficiency was not good, it was previously extremely poor, but continual efforts and improvement in MFCs became the most emerging and excellent way for heavy metals to be treated in conjunction with the present generation. Currently, the design of MFCs is shown to be up to 100% elimination rate, and in certain circumstances to be up to 99% chemical oxygen demand. This type of performance shows that MFCs are sustainable methods of water treatment [61]. The Cu^{2+} metal is extremely appealing when it is recovered or removed since it is commonly used in household, industrial and commercial wastewater. The large potential for decrease via MFCs may readily eliminate copper [62]. The MFCs provide the chance to create electricity and clean wastewater. The MFC process is directly related to the creation of energy and water treatment. Some difficulties occur during operations of MFCs, however, they include poor removal capabilities, lower power generation and extremely costly [63]. For example, researchers could create membranes less MFCs by use of highly efficient electric materials to increase energy generation and metal degrading efficiency. This is because the synthesis of electrons and the development of bacteria depend on energy and metal recovery. The insertion of good electrons can improve these two variables because an outstanding electrode material can give a wider surface for enhanced bacterial metabolism and improve electron production. The carbon-derived materials are used as electrodes in MFCs quite actively. In the early years, however, carbon was shown to have some traces of poorer electric conductivity and fewer microbial colonization surface [64]. A novel allotrope of carbon termed graphene, demonstrating a high bacterial growth surface, high conductivity and mechanically and thermally extremely stable compared to existing carbonic materials, was recently developed by scientists [65, 66]. Thus, it is a highly unique and excellent material to improve the efficiency of MFC's working process in relation to metal degradation/removal and energy generation. These metal ions, which have a detrimental effect on the efficacy of MFCs, are declared extremely deadly to microorganisms/microbes such as nickel, copper, cadmium, mercury, lead and others [67]. Kim et al. [60] studied the inhibition ratio, it was recorded, i.e. 46%, 28%, respectively, used a 1 mg/L Pb^{2+} and 1 mg/L Cd^{2+} synthetic waste water sample. In the original wastewater with 1 mg/L Pb^{2+} and 1 mg/L Cd^{2+} solutions, the inhibition ratio was also considerably higher (76%). However, MFCs demonstrated an assured degree of tolerance at low heavy metal concentrations. Stein et al. [68] revealed that the high potential and current density of various devices such as sensors are generated by lower toxicity levels [69]. The immediate reaction to harmful heavy metals therefore leads to biomonitor functioning [70]. In 2019, the Cr (VI) rehabilitation, which due to its toxicity and high mobility is mostly concentrated in heavy

metal, was reported by Zhang et al. [71]. A novel MFC adsorption reactor combination was created utilizing chromium remedial Platanus acerifolia leaves. Anaerobic loam was employed as a material for the inoculum. At the first 50 mg/L concentration, the removal efficiency was recorded after 16 h of response, 98%. The response was performed at pH 2. Many efforts on chromium removal have been recorded because it is commonly found in wastewater. The study of Fang Li et al. [72] on chromium elimination from waste water was also reported. The objective was to convert a highly hazardous Cr(VI) to a low level of Cr(III). The catholyte buffer solutions impacted the process of reducing chromium. The Cr(VI) removal rate rose to 99.9% at pH 2 with the addition of potassium hydrogen phosphate (KH_2PO_4). The initial amount was 100 mg/L and 52.1 mW/cm^2 was generated. Both study groups utilized carbon felt electrodes for the anode and cathode, and approximately 99.9% have been taken out but the biggest problem is that they did not have enough energy to overcome energy crises. The effectiveness of MFCs in metals with varied parameter effects and energy generation was demonstrated by different studies in terms of their removal/recovery in Table 1. Another study group has been published by Ravinder Kumar et al. [73] for chromium removal by utilizing various states and materials. They obtained excellent energy efficiency, i.e. 970 mW/m^2 using electrode graphite material. Anaerobic sludge has been activated. After 2 h, chromium removal rate was detected at a high output rate of 76% at pH 7 with starting concentration of 20 mg/L. While the rate of removal rose from about 76–94%, the output energy dropped to 6.4 W/m^3 from the initial 970 mW/m^2 with a beginning concentration of 10 mg/l. Substrate utilization is highly important for bacterial development since it is important to degrade the initial inoculum concentration by bacterial capacity. For improved metal removal the appropriate pH, substrates and starting inoculum concentration. Rayu et al. [74] have also shown chromium removal and exhibited a distinct rate of concentration in heavy metals removal effectiveness. The original inoculum concentration was 5 mg/L with clearance effectiveness of 93%, whereas 61% was found in 25 mg/L. The electrode consisted of felt graphite (anode and cathode). *Actinobacteria*, *B-proteobacteria* were conscientiously shown to degrade at (5 mg/L) initial concentrations after 143 h; however, after 2 pm, microorganisms were treated at 192 h in an inoculum sample of 25 mg/L and were shown to be less efficient. The work on reduced graphene oxide was conducted by Yining Wu et al. [75]. The reduced graph oxide is a modified version of graphene oxide. This work demonstrated how graphene oxide was decreased to improve the recovery of copper and energy generation as a cathodic catalyst in MFCs having no permeable membrane in the system. The results showed that the decreased electrode of the graphene cathode offers superior transportation capacity to standard graphene oxide. The energy production was 67% better than other materials and the efficiency of copper degradation was 43% better than graphene oxide. Initial concentration, pH, temperature and electrodes were shown to be extremely critical parameters for improving energy generation. The interspecies synergy of bacteria to resourceful electricity and copper recovery is indicated by Pseudomonas and Geobacter. The toxic metal along with the power outcomes from low wastewater concentrations

Table 1 Metal removal through MFCs with their power output

Metal pollutant	Inoculum source/microbes	Anode electrodes	Cathode electrodes	Operating time	Initial Conc. (mg/L)	Removal Efficiency (%)	Power efficiency	References
Cr^{6+}	Anaerobic sludge	Carbon fibre felt	Carbon fibre felt	240 h	100	75.4 ± 1.9	970.2 ± 60.5 mW/m^2	Zhang et al. [87]
V^{5+}	Anaerobic sludge	Carbon fibre felt	Carbon fibre felt	240 h	100	67.9 ± 3.1	970.2 ± 60.5 mW/m^2	Zhang et al. [87]
V^{5+}	Anaerobic granular sludge	Carbon fibre felt	Carbon fibre felt	72 h	25 mL	87.9	578.3 mW/m^2	Zhang et al. [88]
Cr^{6+}	Domestic wastewater	Graphite plates	Graphite plates	150 h	100	100	150 mW/m^2	Wang et al. [89]
Cr^{6+}	*Shewanella decolorationis S12, K. pneumonia*	Carbon felt	Carbon felt	3.5 h	10	99.9	52.1 mW/cm^2	Li et al. [72]
Cr^{6+}	*Shewanella oneidensis MR-1*	Graphite felt	Graphite rod	192 h	200	67	32.5 mA/m^2	Xafenias et al. [79]
Cr^{6+}	*Indigenous* bacteria from Cr(VI)	Graphite plate	Graphite granular	173 h	39.2	2.4 ± 0.2 mg g VSS^{-1} /h	6.9 A/m^3	Huang et al. [90]
Cr^{6+}	Algae biomass	Activated charcoal	Activated charcoal	96 h	200 mL	98	207 mW/m^2	Singhvi and Chhabra [80]
Cr^{6+}	*Actinobacteria, B-Proteobacteria*	Graphite felts	Graphite felts	144 and 192 h	5 and 25	93 and 61	0.5–0.6 V	Ryu et al. [74]
Cr^{6+}	Anaerobic sludge	Unpolished graphite plate	Natural rutile-coated polished graphite	26 h	26	97	0.55 V	Li et al. [91]

(continued)

Table 1 (continued)

Metal pollutant	Inoculum source/microbes	Anode electrodes	Cathode electrodes	Operating time	Initial Conc. (mg/L)	Removal Efficiency (%)	Power efficiency	References
Ag^{+}	Sludge mixture	Carbon brush	Carbon cloth	8 h	50–200 ppm	99.91	4.25 W/m^2	Choi and Cui [92]
Au^{3+}	*Shewanella genus*	Pt-graphite	Pt-graphite	–	200 ppm Au with 1,000 ppm standard solutions of HAuCl4	60	0.6–0.2 V	Varia et al. [81]
Cu^{2+}	Anaerobic sludge	Graphite felt	Graphite plate	144 h	500	70	314 mW/m^3	Tao et al. [93]
CN^{-}	*Klebsiella sp. MC-1*	Carbon cloth	Carbon cloth	75 h	50	99.1	412 mV	Ya-Li et al. [94]
Cd^{3+}, Zn^{2+}	Sewage sludge	Carbon cloth (no wet proofing)	carbon cloth (30% wet proofing)	–	200 mM Cd; 400 mM Zn	Cd 90 Zn 97	3.6 W/m^2	Abourached et al. [82]
Au^{3+}	Tetrachloroaurate wastewater	Carbon brush	Carbon cloth	12 h	2,000 ppm	99.89 ± 0.00	6.58 W/m^2	Choi and Hu [95]
Ag^{+}	NH_3 chelated silver waste water	Carbon cloth	Graphite	21 h	–	99.9	317 mW/m^2	Wang et al. [96]
Cr^{6+}	Anaerobic cultures mixed with Cr (VI)	Graphite plate	Graphite plate	45 days	80	0.46 mg Cr (VI)/g VSS·h	55.5 mW/m^2	Tandukar et al. [97]
Co^{2+}	Lithium cobalt oxide Solution	Graphite felt	Graphite felt	–	200	62.5 ± 1.8	298 ± 31 mW/m^3	Huang et al. [98]
Pt	Anaerobic sludge bed	Graphite plate	Graphite plate	24 h	16.88	90	844.0 mW/ m^2	Liu et al. [84]

(continued)

Table 1 (continued)

Metal pollutant	Inoculum source/microbes	Anode electrodes	Cathode electrodes	Operating time	Initial Conc. (mg/L)	Removal Efficiency (%)	Power efficiency	References
V^{5+}	*Dysgonomonas* and *Klebsiella*	Carbon fibre felt	Carbon fibre felt	7 days	200	60.7	529 ± 12 mW/m^2	Qiu et al. [83]
Cr^{6+}	Anaerobic digestion sludge	Carbon felt	Carbon felt	16 h	50	98	343 mV	Zhang et al. [71]
Cu^{2+}	Anaerobic sludge with copper	Graphite felt	Graphite plate	144 h	500	70	314 mW/m^3	Tao et al. [93]
Cu^{2+}	*Geobacter* and *Pseudomonas,*	Carbon brush	Reduced Graphene oxide	–	12	98	0.95 W/m^2	Wu et al. [75]
Cr^{6+}, Cd^{2+}	Anerobic pure culture	Carbon rod	Graphite felt	24 h	Cr (VI) 385 µM, Cd (II) 179 µM	73 (Cr), 61 (Cd)	14.2 mW/m^2	Huang et al. [77]
Hg^{2+}	Anaerobic sludge	Graphite felt	Carbon paper	10 h	100	98.22–99.54	433.1 mW/m^2	Wang et al. [99]
Toxic thallium (TI)	Anaerobic sludge	Carbon felt	Plain carbon paper	72 h	100 µg/L	67	457.8 ± 15.2 mWm^{-2}	Wang et al. [85]
Cr^{3+}	Anaerobic sludge	Graphite brushes	Graphite granules	–	10	94	6.4 W/m^3	Kumar et al. [73]
Cr^{3+}	Primary clarifier effluent	Graphite brushes	Graphite granules	2 h	20	76	970 mW/m^2	–
Cr^{3+}	–	Carbon brush	Carbon cloth	–	100	99	419 mW/m^2	–
Ammonia-Cu^{2+}	Activated sludge	Graphite felt	Graphite plate	28 days	100	96	140 mW/m^2	–

(continued)

Table 1 (continued)

Metal pollutant	Inoculum source/microbes	Anode electrodes	Cathode electrodes	Operating time	Initial Conc. (mg/L)	Removal Efficiency (%)	Power efficiency	References
V^{5+}	–	Carbon fibre felt	Carbon fibre felt	–	–	68	970 mW/m^2	–
Zn^{2+}	Activated sludge	Carbon cloth	Carbon cloth	–	–	97	3600 mW/m^2	–
Cu^{2+}	Anaerobic sludge	Graphite plate	Graphite plate	20 h	6412.5 ± 26.7 mg Cu^{2+}/L	>99	339mW/m^3	Tao et al. [100]
Cu^{2+}, Pb^{2+}	Dilute synthetic sample	Carbon felt	Carbon felt	14–36 days	1.1 mg/L Cu^{2+}, 2.5 mg/L Pb^{2+}	92 (Pb), 99 (Cu)	17.1–25.2 mA	Modin et al. [101]
Cd^{3+}, Zn^{2+}	Dilute synthetic sample	Carbon felt	Carbon felt	56 days	7.4 19.5	82 (Cd) 89 (Zn)	–	–
Cd^{6+}	Contaminated soil	Graphite granules	Carbon felt	143 days	100	31	7.5 mW/cm^2	Habibul et al. [78]
Pb^{2+}	Contaminated soil	Graphite granules	Carbon felt	108 days	900	44.1	3.6 mW/cm^2	–
Cu^{2+}	Anaerobic sludge bed	Carbon brush	Carbon cloth	5 h	12.5	98.3	0.2 W/m^3	Wu et al. [62]
V^{5+}	Anaerobic sludge	Carbon fibre felt	Carbon fibre felt	72 h	500	25	0.572 W/m^2	Nancharaiah et al. [76]
Ag^{+}	Anaerobic sludge	Carbon cloth	Graphite felt	21 h	1000	99	0.3 W/m^2	–
Ag^{+}	Anaerobic sludge	graphite plate	Graphite felt	26 h	200	95	0.109 W/m^2	–
Ag^{+}	Anaerobic sludge	Carbon brush	Carbon cloth	8 h	200	99	4.25 W/m^2	–

(continued)

Table 1 (continued)

Metal pollutant	Inoculum source/microbes	Anode electrodes	Cathode electrodes	Operating time	Initial Conc. (mg/L)	Removal Efficiency (%)	Power efficiency	References
Se	Anaerobic sludge	Carbon cloth	Carbon cloth	48 h	75	99	2.90 W/m^2	–
Au^{3+}	–	Carbon brush	Carbon cloth	–	200	99.8	6.58 W/m^2	–
Co^{2+}	Anaerobic sludge	Graphite felt	Graphite felt	48 h	1000	99.15	–	–
Cr^{6+}	Anaerobic sludge	Graphite plates	Graphite plates	150 h	200	100	0.150 W/m^2	–
Cr^{6+}	Anaerobic sludge	Graphite plates	Graphite plates	26 h	26	97	–	–
Cr^{6+}	Anaerobic sludge	Carbon cloth	Carbon cloth	48 h	100	99	0.767 W/m^2	–
Cu^{2+}	–	Graphite plate	Graphite foil	6 days	1	99.8	0.80 W/m^2	–
Cu^{2+}	Anaerobic sludge	Graphite felt	Graphite felt	–	10–200	>99	0.319 W/m^2	–
Ni^{2+}	Anaerobic sludge	Graphite felt	Graphite plate	24 h	26.4	95	0.68–0.7 V	Liu et al. [102]
Ni^{2+}	Mixed microbial culture	Graphite felt	Graphite felt	30 days	32.9 g/180 ml	–	150–200 m W/m^2	Gai et al. [60]
Cd^{6+}	Mixed microbial culture	Graphite felt	Graphite felt	7 days	50 mg/ml	60	700–750 mW/m^2	–
Hg^{6+}	Mixed microbial culture	Graphite felt	Graphite felt	15 days	25 mg/ml	55	800 mW/m^2	–

from the microbial fuel cell will be extremely important. Graphite felt as electrodes for heavy metals comprising Cu, Ni and Hg is used by Ruizhe Gai et al. [60]. They examined the parameter of concentration to study how to link concentration influences power performance. They observed a high-voltage output at low concentrations, while the current density was lowered when the concentration grew. The energy yield and inoculum concentration are inversely related. Ruishe has also changed response time by treating Ni for 30 days and obtaining 150–200 mW/m^2, Cd and Hg for 7 and 15 days and attaining 60–55% elimination rates, i.e. 700–750 and 800 mW/m^2 power output. Nancharaiah et al. [76] have emphasized that metal wastes and their pollutions represent a major danger to the environment of man and second waste water contains extremely precious metals for recovery. They opted to utilize graphite felt material for the treatment of copper from wastewater as anode and cathode. The study indicated that many parameters such as temperature, length of reaction, first concentration, etc., were analysed. With acidic state, the removal rate was 99% at 144 h and with time, the initial concentration rose to 480 h at concentrations of 200–600 mg/L, removal efficiency also quietly perturbed and fell from 99%. At 144 h with a lesser starting concentration, the density was considerably better than 480 h with high concentration. The dual Cd(II) and Cr(VI) degradation from the MFCs-catholyte were employed for Huang et al. [77]. The efficiency for removal of chromium from anaerobic purity was recorded at 73% and cadmium at 61% by utilizing graphite felt for the cathode, while the anode is a carbon rod in MFCs double-chamber system. The output power density was 14.2 mW/m^2 and the procedure was performed within 24 h and under 5.8–6 pH. Efficiency of removal is much better, but energy output was not excellent, thus it is strongly advised that different materials be used in order to compose and increase energy production as well as efficiency of removal. The potential for on-site electrokinetic heavy metal treatments was investigated by Habibula et al. [78]. Following 143 days, the results indicated very low power generation and low efficiency. The energy generation was 7.7 mW/m^2 and the contaminated soil sample was removed only 31% with the use of graphic granule as anode that could not produce active electron flows. The *Shewanella oneidensis MR-1* as the system's catalyst, and lactate as a substratum for strengthening *Shewanella oneidensis MR-1* growth was shown in the performance of Cr(IV) Bu by Xafenias et al. [79]. The percentage of elimination obtained was 67% together with the output of 32.5 mA/m^2. The operating duration of MFCs was 192 h at an initial pH of 200 mg/L. The research groups of Xafenias utilized graphical graphics as electrodes to give *Shewanella oneidensis MR-1* sufficient growth for greater reduction. The other side Singhvi et al. [80] have found that the elimination of chromium is 98% utilizing activated charcoal as algal biomass electrodes. The group obtained high energy output of Xafenias et al. (207 mA/m^2 and greater removal rates) because Xafenias and Singhvi et al. utilized neutral pH range while Xafenias used an acidic environment. In terms of removal or deterioration, the pH is highly significant. The less acidic environment does not enable bacteria to more efficiently breakdown the metal. The electrodeposition of precious metal gold by the electroactive Shewanella genus on Pt-graphite electrodes has been studied by Varia et al. [81]. The original use was 200 ppm, and the removal rates were 6% with a current density of 0.6 to −

0.2 V. Cyanide degrading bacterium known as *Klebsiella sp. MC-1* has been utilized by Wang et al. [82] to reduce cyanide from anaerobic sludge. The findings indicated an improvement of 99.1% at 412 mV with a high degradation efficiency. Coal was used as electrodes at a temperature of 25–50 °C, pH of 5 and an initial concentration of 50 mg/L. A competent technique for vanadium degradation from polluted water has been described by Rui Qiu et al. [83]. Here, MFCs application in the reduction of vanadium and bioenergy generation using biocathode carbon fibre felt full remediation of V(V) at an initial concentration of 200 mg/L within 7 days was the result of electrochemical and bacterial reductions. The energy density attained was recorded to be 529 ± 12 mW/m^2. Liu et al. [84] have examined the conversion of platinum and distribution in MFCs and have demonstrated a viable method towards the degradation of platinum from polluted water and the production of Pt/C catalyst to MFCs. The result showed 90% that the starting concentration of 16.88 mg/L produces a silent high density of 844.0 mW/m^2. The outcome was 90%. MFCs' extremely hazardous thallium (Tl) removal performance was reported by Zhongli et al. [85] since worldwide focus is paid to developing important thallium removal procedures more effectively. Tl(I) was spontaneously oxidized in MFCs. For 72 h the removal effectiveness was 67%, with a starting amount of 100 μg/L. Therefore, a max. power density, recorded 457.8 ± 15.2 mW/m^2 was shown. The electrochemical method described some negative energy output effects of thallium. After oxidation, the product was less mobile and might reasonably fall in pH series. In particular, in cases of thallium, the MFCs are highly efficient for treating wastewater contaminants. This proposal could be beneficial for researchers using high-surface materials such as graphene oxide, reduced graphene oxide or nanocomposites which have shown outstanding removal capability [86].

4 Other Application of MFCs

MFC is a very famous and meaningful electrochemical instrument that converts organic energy directly into electricity. This procedure is performed with several kinds of bacteria utilizing biocatalyst. It makes it prolific with the various active catalytic activity of microorganisms. However, two electrodes, cathode and anode, are present in the MFCs. The MFCs are operated in the presence of a permeable exchange membrane or a salt bridge, in order to transfer protons and electrons from the outside route, although the MFCs may be operated with no membrane and less MFC membrane. Protons of this sort of MFCs are sent without help directly to the cathode chamber. During operation, MFCs electrodes function as an electron receiver. MFCs may oxidize completely fuels such as industrial, wastewater swage, substrates (acetate, glucose, sugar, etc.) Reducing the usage of fossil fuels is a major problem worldwide. In addition, the European Council on Renewable Energy said that in 2040, over 50% of renewable green energy consumption will be produced

by virtue of their potential and important characteristics [103]. The possible benefits of MFCs include wastewater treatment, energy supply, economic sustainability and environmental stability [104].

4.1 Bioenergy Production

MFCs are mostly utilized for the present generation, and many attempts have been made in improving the current generation using MFCs as seen in Table 1. In anode compartment, the biocatalyst (microbials) oxidizes the organic substrate for electrons and protons [47, 105, 106]. With the use of externally supplied circuit and proton, the electron is transferred into the cathode chamber by means of a salty or permeable bridge or by transfer to the cathode chamber directly [107]. Both chambers have a multimeter and resistor box electrically linked. The box with many metres and resistors was intended to measure the current. MFCs mainly adjust exoelectrogens surrounding the anode and created a biofilm on the area of anode electrode to the primary phase of present production. Exoelectrogens thus create a leading biofilm that has a thickness of a few micrometres [108]. Exoelectrogens formation of biofilm is unique and differs from bacteria. If the electron reaches the cathode, the electron receiver and protons might react. Subsume that the product was water, with maximum current, i.e. ~0.805 V seen on a cathodic electrode if oxygen was an electron acceptor in the cathode chamber Normally, with any selected catalyst, the cathode surface is changed to improve oxygen reduction. Titanium, copper and platinum are the preferred catalyst. For example, at varying concentrations, platinum/carbon composite electrodes are made available [109]. Scientists in area of bio-electrochemical research are currently highly engrossed with findings concerning the development of MFCs. Scholars in this field are putting greater focus to find more effective material to introduce in MFCs to develop greater energy output [110]. Many of the researchers used various parameters and developed various configuration styles for MFCs to study the improvement in bioenergy production as shown in Table 1. There was a different material used, and due to different efforts, different energy was achieved by researchers. The key to improving energy production is studying very crucial MFCs parameters to achieve them at cheap costs. The pH, exoelectrogens, substrate, temperature and electrode material are the major factors. MFCs design. It is intended to provide you better results to enhance the electrode material by composite with other materials and to manage the pH solution at the desired temperature [111].

4.2 Bioelectronics Devices

MFCs carried some significant values in the field of bioelectronics to make more reliable devices for human beings. The electrical active microbes may take substantial value in bioelectronics field because they have ability to sense different types of

chemicals and environmental conditions. The sense response can be interpreted into electric signal form, which may lead to advance biocomputing and biological sensors. The most important and valuable factor is the conductivity of microbe's biofilms and the action of microbe pili which are conductive in nature, may lead to new research direction for the development of different electronic systems also called living electronic device by using these materials. Electronic devices prepared by using the living components carried out some novel advantage such as charge are storable and easily transferable under the water, electronic devices can be constructed from low cost and low toxic feedstock without producing high waste material, living electronic devices has the ability for self-repairing and replication, useful in medical instrumentation due to bacterial can transfer electrons to electrode easily [33]. G. sulfurreducens has high conductivity that makes them more favourable and convenient as supercapacitors than as other lesser self-discharging artificial supercapacitors. Microorganism with different component conductivity can be operated by genetic engineering technology. G. sulfurreducens biofilms can be served as logic devices such as transistors and many others.

4.3 Biosensor

The MFC technology is also used as biosensor, even though there were a lot of reported works on generation of electricity, removal, recovery of metals from wastewater, organic pollutant removal dyes removal, etc. MFC devices served as sensor for the detection of different pollutants in water. The biosensor which is based on MFC working principle shows many advantages over traditional biosensors [112]. These advantages are high stability, good reliability, eco-friendly, low cost, high accuracy, etc. MFC biosensor also don't need any type of transducer which are mostly used in traditional biosensors [113]. Furthermore, MFC biosensors don't need any high maintenance and they can be work for long period without any maintenance problems. MFC-based sensors can work in two different modes. The first mode is the flow-through electrode and the other is flow-by electrodes. In the first mode, the porous electrode passed out the water sample, while another mode, the water material moves parallel to surface of electrode [114]. The MFC sensor operation through these two paths can enhance the diffusion and electrolytes of the ions, thus increasing the MFC-based sensor sensitivity for better outcomes. Furthermore, it was reported that anode flow in MFC sensor also helps to increase the proton diffusion by anodic biofilm, improving the substrates by using exoelectrogens. Obviously, the MFC toxic sensor sensitivity was improved roughly 40 times due to flow through anode than flow-by anode. The duel electrodes of MFC are employed for the improvement of biosensors but the reliability and stability of duel electrodes are still at the improving stage [115].

5 Future Perspectives

MFCs are a scientific interest, it provides an opportunity to produce safe, eco-friendly and renewable energy along with water treatment simultaneously. Numerous wastewaters fluctuating from low to higher strength have been used for wastewater treatment in MFCs and are capable to generate electricity simultaneously. Despite all development, still, the energy outputs were found low through MFCs. The world is looking for renewable energy to overcome the future perspective, scientific scholar should focus to improve an appropriate design for MFCs, use those materials which has ability to improve the electron transfer mechanism, prefer genetically engineered microbes for operation, use treated inoculum, reduce start-up duration for MFCs, prefer good electrode material (high conductive, high surface area, high thermally and mechanical stable, etc.) [27]. Further, effective wastewater treatment can be done by MFCs at 20 and 45 °C temperatures. Additionally, MFCs combined with anaerobic fermentation technology to enhance the COD removal rate. Substantial efforts have been devoted to scale up the design of MFC device, e.g. MFCs with 90 L volume gained the highest reduction of COD, i.e. ~87% with inoculum brewery wastewater [116]. It has revealed an excessive potential for heavy metals or toxic pollutants to remove or reduced from wastewater. The high redox potential heavy metals are gaining high interest to serve as an electron acceptor, to produce high current density from MFCs. Wang et al. [117] achieved 100% removal efficiency of chromium from domestic wastewater by using double chamber MFCs with the utilization of graphitic electrodes. The density of power generated was 150 mW/m^2. The MFC device is also capable of applied as biosensor (COD or BOB) to detect the toxic and lethal pollutants present in wastewater. The MFC application for biosensor is currently engulfed with certain challenges like poor consistency, inadequate sensitivity and poor accuracy. These problems might be possible to solve by operating the flow-through mode. The MFCs have been explored for several applications. Although there were some specific challenges and problems. These need to be improved or solved to make this technique more prolific. MFC technology is not still useable at a commercial scale even with more than 10 years of exhaustive study on the MFCs [118]. There is still a gap present to launch in world practically at commercial level. The major drawback of this technique is inadequate power generation and high-cost issue of material making it uncomfortable for commercial level. The energy output and wastewater treatment can be achieved able by using low-cost material like use waste material for electrode synthesis, use cheap binders to reduce cost issues. Another hindrance is the selection of electron acceptor at cathode electrode. The most efficient and effective choice is oxygen for electron acceptor, and it is abundantly available but constant oxygen sparging on cathode can damage the microbial community activities at anode. Pt is commonly utilized for oxygen reduction reaction, but the cost of Pt is very high, so it is unfit and required any other alternative. The sensor application is not well explored because MFC-based sensors' response time is too longer than others and the other problem is produced energy is not efficient to run sensor operations constantly in an effectively way [119]. This portion should be concentrated on

the scientific community to investigate its biosensor qualities since the detector can readily identify different pollutants. The procedure is straightforward and cheap.

6 Conclusion

This chapter has made every effort to elucidate the importance of MFCs in the removal of dyes, organic, inorganic and heavy metals found in wastewater by using progressive and low-cost material, so it can serve as a useful read for scholars to extrapolate ideas about different available costless materials capable of improving the working performance of MFCs. MFC is a trending and novel technology to generate electricity from biowastes by using microorganisms as biocatalyst. The major focus of this article is to develop an adequate understanding for readers in MFCs towards improving their research work. This study was conducted on previously reported research within 10–12 years back, what improvements people already made, etc. In spite of all improvements, there are identified research gaps present such as the production efficiency of energy but produced power outcomes from MFCs is too poor yet, MFCs can serve as biosensor, but very little work was reported regarding MFC-based biosensor. MFC technology is still inadequate method to use for commercial purpose despite rigorous research efforts over the years. There is still a need for more efforts to launch MFCs around the world at a practical scale. The bioremediation of organic pollutant and heavy metals was quite great in few cases, and it was observed that there are some parameters which are affecting bioremediation and energy generation process, i.e. pH, temperature, concentrations, substrate type, activity of microbes and most especially is material for electrode. For example, it has been reported in literatures that heavy metal degradation in MFCs was greater at acidic pH, better conductive electrodes giving high degradation results coupled with greater power density output. Another research gap yet to be adequately explored is still in the fabrication of electrodes from biowaste materials. There exist several kinds of waste materials with high carbon content upon carbonization that can be converted into graphene oxide and further develop into electrodes in MFCs. As a result, the choice of these factors is critical for better results. Literature also indicates that modifying the electrodes can improve the removal efficiency of MFCs. The conductive polymer is a popular material used to create composites in order to improve the efficiency and productivity of MFCs. However, there has been little reported effort in this research approach. Furthermore, there is still great scope of research to use low-cost materials in MFCs for better and inexpensive wastewater treatment.

Acknowledgements This chapter was supported by Universiti Sains Malaysia, 11800 Penang Malaysia.

References

1. Yaqoob AA, Parveen T, Umar K, Ibrahim MNM (2020) Role of nanomaterials in the treatment of wastewater: a review. Water 12:495
2. Yaqoob AA, Bakar MA, Kim HC, Ahmad A, Alshammari MB, Yaakop AS (2022) Oxidation of food waste as an organic substrate in a single chamber microbial fuel cell to remove the pollutant with energy generation. Sust Energy Technol Assess 52
3. Ab Razak NH, Praveena SM, Aris AZ, Hashim Z (2015) Drinking water studies: a review on heavy metal, application of biomarker and health risk assessment (a special focus in Malaysia). J Epidemiol Glob Health 5:297–310
4. Ahmad A, Khatoon A, Laskar M, Islam A, Mohammad AW, Yong N (2013) Use of 2-hydroxy-3-methoxybenzaldehyde functionalized amberlite xad-16 for preconcentration and determination of trace metal ions by flame atomic absorption spectrometry. Der Pharma Chem 5:12–23
5. Ong CB, Mohammad AW, Ng LY, Mahmoudi E, Azizkhani S, Hairom NHH (2017) Solar photocatalytic and surface enhancement of ZnO/rGO nanocomposite: degradation of perfluorooctanoic acid and dye. Process Saf Environ Prot 112:298–307
6. Sankhla MS, Kumari M, Nandan M, Kumar R, Agrawal P (2016) Heavy metals contamination in water and their hazardous effect on human health—A review. Int J Curr Microbiol App Sci 5:759–766
7. Slate AJ, Whitehead KA, Brownson DA, Banks CE (2019) Microbial fuel cells: an overview of current technology. Renew Sustain Energy Rev 101:60–81
8. Chuo SC, Mohamed SF, Mohd Setapar SH, Ahmad A, Jawaid M, Wani WA, Yaqoob AA, Ibrahim MNM (2020) Insights into the current trends in the utilization of bacteria for microbially induced calcium carbonate precipitation. Materials 13:4993
9. Azimi A, Azari A, Rezakazemi M, Ansarpour M (2017) Removal of heavy metals from industrial wastewaters: a review. ChemBioEng Rev 4:37–59
10. Uddin MK (2017) A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem Eng J 308:438–462
11. Abdel-Shafy HI, Mansour MS (2016) A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt J Pet 25:107–123
12. Alzahrani S, Mohammad AW (2014) Challenges and trends in membrane technology implementation for produced water treatment: a review. J Water Process Eng 4:107–133
13. Hairom NHH, Mohammad AW, Ng LY, Kadhum AAH (2015) Utilization of self-synthesized ZnO nanoparticles in MPR for industrial dye wastewater treatment using NF and UF membrane. Desalin Water Treat 54:944–955
14. Yaqoob AA, Umar K, Ibrahim MNM (2020) Silver nanoparticles: various methods of synthesis, size affecting factors and their potential applications—A review. Appl Nanosci, 1–10
15. Moradi F, Maleki V, Saleh-Ghadimi S, Kooshki F, Pourghassem Gargari B (2019) Potential roles of chromium on inflammatory biomarkers in diabetes: a systematic review. Clin Exp Pharmacol Physiol
16. Genchi G, Sinicropi M, Carocci A, Lauria G, Catalano A (2017) Mercury exposure and heart diseases. Int J Environ Res Publ Health 14:74
17. Saghazadeh A, Rezaei N (2017) Systematic review and meta-analysis links autism and toxic metals and highlights the impact of country development status: higher blood and erythrocyte levels for mercury and lead, and higher hair antimony, cadmium, lead, and mercury. Prog Neuropsychopharmacol Biol Psychiatry 79:340–368
18. Yaqoob AA, Ahmad H, Parveen T, Ahmad A, Oves M, Ismail IM, Qari HA, Umar K, Ibrahim MNM (2020) Recent advances in metal decorated nanomaterials and their various biological applications: a review. Front Chem 8:341
19. Rajeswari TR, Sailaja N (2014) Impact of heavy metals on environmental pollution. J Chem Pharm Sci 3:175–181

20. Bashir MJ, Amr SSA, Aziz SQ, Aun NC, Sethupathi S (2015) Wastewater treatment processes optimization using response surface methodology (RSM) compared with conventional methods: review and comparative study, Middle-East. J Sci Res 23:244–252
21. Yaqoob AA, Noor M, Serrà A, Ibrahim MNM (2020) Advances and challenges in developing efficient graphene oxide-based ZnO photocatalysts for dye photo-oxidation. Nanomaterials 10:932
22. Yaqoob AA, Umar K, Adnan R, Ibrahim MNM, Rashid M (2021) Graphene oxide-ZnO nanocomposite: an efficient visible light photocatalyst for degradation of rhodamine B. Appl Nanosci 11:1291–1302
23. Ahmad A, Setapar SHM, Yaqoob AA, Ibrahim MNM (2021) Synthesis and characterization of GO-Ag nanocomposite for removal of malachite dye from aqueous solution. Mater Today: Proc
24. Basri S, Kamarudin SK (2019) Microbial fuel cell (MFC) variants, waste to sustainable energy: MFCs—Prospects through prognosis
25. Behera BK, Varma A (2016) Microbial fuel cell (MFC). In: Microbial resources for sustainable energy. Springer, pp 181–221
26. Salar-García MJ, Gajda I, Ortiz-Martínez VM, Greenman J, Hanczyc M, de Los Ríos A, Ieropoulos I (2016) Microalgae as substrate in low cost terracotta-based microbial fuel cells: novel application of the catholyte produced. Bioresour Technol 209:380–385
27. Rahimnejad M, Adhami A, Darvari S, Zirepour A, Oh S-E (2015) Microbial fuel cell as new technology for bioelectricity generation: a review. Alex Eng J 54:745–756
28. Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40:5181–5192
29. Kim K-Y, Yang W, Logan BE (2015) Impact of electrode configurations on retention time and domestic wastewater treatment efficiency using microbial fuel cells. Water Res 80:41–46
30. Yaqoob AA, Ibrahim MNM, Yaakop AS, Umar K, Ahmad A (2020) Modified graphene oxide anode: a bioinspired waste material for bioremediation of Pb2+ with energy generation through microbial fuel cells. Chem Eng J, 128052
31. Song T-S, Wang D-B, Wang H, Li X, Liang Y, Xie J (2015) Cobalt oxide/nanocarbon hybrid materials as alternative cathode catalyst for oxygen reduction in microbial fuel cell. Int J Hydrog Energy 40:3868–3874
32. Palanisamy G, Jung H-Y, Sadhasivam T, Kurkuri MD, Kim SC, Roh S-H (2019) A comprehensive review on microbial fuel cell technologies: processes, utilization, and advanced developments in electrodes and membranes. J Clean Prod
33. Abbas SZ, Rafatullah M, Ismail N, Syakir MI (2017) A review on sediment microbial fuel cells as a new source of sustainable energy and heavy metal remediation: mechanisms and future prospective. Int J Energy Res 41:1242–1264
34. Santoro C, Arbizzani C, Erable B, Ieropoulos I (2017) Microbial fuel cells: from fundamentals to applications. A review. J Power Sour 356:225–244
35. Mustakeem M (2015) Electrode materials for microbial fuel cells: nanomaterial approach
36. Yaqoob AA, Ibrahim MN, Ahmad A, Khatoon A, Setapar SH (2021) Polyaniline-based materials for supercapacitors. In: Handbook of supercapacitor materials: synthesis, characterization, and applications, pp 113–130
37. Umar K, Yaqoob A, Ibrahim M, Parveen T, Safian M (2020) Environmental applications of smart polymer composites. Smart Polym Nanocompos Biomed Environ Appl 15:295–320
38. Yaqoob AA, Ibrahim MNM, Rodríguez-Couto S (2020) Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview. Biochem Eng J 164:107779
39. Yaqoob AA, Serrà A, Ibrahim MNM, Yaakop AS (2021) Self-assembled oil palm biomass-derived modified graphene oxide anode: an efficient medium for energy transportation and bioremediating Cd (II) via microbial fuel cells. Arab J Chem 14:103121
40. Yaqoob AA, Guerrero–Barajas C, Ibrahim MN, Umar K, Yaakop AS (2022) Local fruit wastes driven benthic microbial fuel cell: a sustainable approach to toxic metal removal and bioelectricity generation. Environ Sci Pollut Res 12:1–6

41. Idris MO, Kim HC, Yaqoob AA, Ibrahim MNM (2022) Exploring the effectiveness of microbial fuel cell for the degradation of organic pollutants coupled with bio-energy generation. Sust Energy Technol Ass 52:102183
42. Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C (2021) Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov, 101579
43. Watts MP, Coker VS, Parry SA, Pattrick RA, Thomas RA, Kalin R, Lloyd JR (2015) Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr(VI) leachate and chromite ore processing residue. Appl Geochem 54:27–42
44. Hao L, Zhang B, Tian C, Liu Y, Shi C, Cheng M, Feng C (2015) Enhanced microbial reduction of vanadium (V) in groundwater with bioelectricity from microbial fuel cells. J Power Sour 287:43–49
45. Wang K, Liu Y, Chen S (2011) Improved microbial electrocatalysis with neutral red immobilized electrode. J Power Sour 196:164–168
46. Fadzli FS, Rashid M, Yaqoob AA, Ibrahim MNM (2021) Electricity generation and heavy metal remediation by utilizing yam (Dioscorea alata) waste in benthic microbial fuel cells (BMFCs). Biochem Eng J 172:108067
47. Yaqoob AA, Ibrahim MNM, Yaakop AS, Ahmad A (2021) Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. Appl Nanosci 11:1949–1961
48. Daud NN, Ahmad A, Yaqoob AA, Ibrahim MN (2021) Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. Environ Sci Pollut Res, 1–33
49. Fang C, Achal V (2019) The potential of microbial fuel cells for remediation of heavy metals from soil and water—Review of application. Microorganisms 7:697
50. Bian Y, Xiong N, Zhu G (2018) Technology for the remediation of water pollution: a review on the fabrication of metal organic frameworks. Processes 6:122
51. Hu J, Zhang Q, Lee D-J, Ngo HH (2018) Feasible use of microbial fuel cells for pollution treatment. Renew Energy 129:824–829
52. Beyene HD, Werkneh AA, Ambaye TG (2018) Current updates on waste to energy (WtE) technologies: a review. Renew Energy Focus 24:1–11
53. Yaqoob AA, Ibrahim MNM, Umar K, Parveen T, Ahmad A, Lokhat D, Setapar SH (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214:379–389
54. Mathuriya AS (2014) Eco-affectionate face of microbial fuel cells. Crit Rev Environ Sci Technol 44:97–153
55. Liu L, Yang Y, Li DL (2012) Accelerated hexavalent chromium [Cr(VI)] reduction with electrogenerated hydrogen peroxide in microbial fuel cells. In: Advanced materials research. Trans Tech Publ, pp 1525–1528
56. Liu L, Yuan Y, Li F-B, Feng C-H (2011) In-situ Cr(VI) reduction with electrogenerated hydrogen peroxide driven by iron-reducing bacteria. Biores Technol 102:2468–2473
57. Breuer M, Rosso KM, Blumberger J, Butt JN (2015) Multi-haem cytochromes in Shewanella oneidensis MR-1: structures, functions and opportunities. J R Soc Interface 12:20141117
58. Yaqoob AA, Khatoon A, Mohd Setapar SH, Umar K, Parveen T, Ibrahim MNM, Ahmad A, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10:819
59. Liu Y, Shen J, Huang L, Wu D (2013) Copper catalysis for enhancement of cobalt leaching and acid utilization efficiency in microbial fuel cells. J Hazard Mater 262:1–8
60. Gai R, Liu Y, Liu J, Yan C, Jiao Y, Cai L, Zhang L (2018) Behavior of copper, nickel, cadmium and mercury ions in anode chamber of microbial fuel cells. Int J Electrochem Sci 13:3050–3062
61. Mathuriya AS, Yakhmi J (2014) Microbial fuel cells to recover heavy metals. Environ Chem Lett 12:483–494
62. Wu Y, Zhao X, Jin M, Li Y, Li S, Kong F, Nan J, Wang A (2018) Copper removal and microbial community analysis in single-chamber microbial fuel cell. Biores Technol 253:372–377

63. Kirubaharan CJ, Kumar GG, Sha C, Zhou D, Yang H, Nahm KS, Raj BS, Zhang Y, Yong Y-C (2019) Facile fabrication of Au@ polyaniline core-shell nanocomposite as efficient anodic catalyst for microbial fuel cells. Electrochimica Acta 328:135136
64. Do M, Ngo H, Guo W, Liu Y, Chang S, Nguyen D, Nghiem L, Ni B (2018) Challenges in the application of microbial fuel cells to wastewater treatment and energy production: a mini review. Sci Total Environ 639:910–920
65. Yaqoob AA, Ibrahim MNM, Ahmad A, Reddy AVB (2021) Toxicology and environmental application of carbon nanocomposite. In: Environmental remediation through carbon based nano composites. Springer, pp 1–18
66. Kanwal A, Yaqoob AA, Siddique A, Bhawani SA, Ibrahim MNM, Umar K (2021) Hybrid nanocomposites based on graphene and its derivatives: from preparation to applications. In: Graphene and nanoparticles hybrid nanocomposites: from preparation to applications, 261
67. Yaqoob AA, Fadzli FS, Ibrahim MNM, Yaakop AS (2022) Benthic microbial fuel cells: a sustainable approach for metal remediation and electricity generation from sapodilla waste. Inter J Environ Sci Technol 10:1–4
68. Stein NE, Hamelers HV, Buisman CN (2012) Influence of membrane type, current and potential on the response to chemical toxicants of a microbial fuel cell based biosensor. Sens Actuat B Chem 163:1–7
69. Yu D, Bai L, Zhai J, Wang Y, Dong S (2017) Toxicity detection in water containing heavy metal ions with a self-powered microbial fuel cell-based biosensor. Talanta 168:210–216
70. Ivars-Barceló F, Zuliani A, Fallah M, Mashkour M, Rahimnejad M, Luque R (2018) Novel applications of microbial fuel cells in sensors and biosensors. Appl Sci 8:1184
71. Zhang T, Hu L, Zhang M, Jiang M, Fiedler H, Bai W, Wang X, Zhang D, Li Z (2019) Cr(VI) removal from soils and groundwater using an integrated adsorption and microbial fuel cell (A-MFC) technology. Environ Pollut
72. Li F, Jin C, Choi C, Lim B (2019) Simultaneous removal and/or recovery of Cr(VI) and Cr(III) using a double MFC technique. Environ Eng Manag J (EEMJ) 18
73. Kumar R, Singh L, Zularisam A, Hai FI (2018) Microbial fuel cell is emerging as a versatile technology: a review on its possible applications, challenges and strategies to improve the performances. Int J Energy Res 42:369–394
74. Ryu EY, Kim M, Lee S-J (2011) Characterization of microbial fuel cells enriched using Cr(VI)-containing sludge. J Microbiol Biotechnol 21:187–191
75. Wu Y, Wang L, Jin M, Kong F, Qi H, Nan J (2019) Reduced graphene oxide and biofilms as cathode catalysts to enhance energy and metal recovery in microbial fuel cell. Biores Technol 283:129–137
76. Nancharaiah Y, Mohan SV, Lens P (2015) Metals removal and recovery in bioelectrochemical systems: a review. Biores Technol 195:102–114
77. Huang L, Zhou P, Quan X, Logan BE (2018) Removal of binary Cr(VI) and Cd (II) from the catholyte of MFCs and determining their fate in EAB using fluorescence probes. Bioelectrochemistry 122:61–68
78. Habibul N, Hu Y, Sheng G-P (2016) Microbial fuel cell driving electrokinetic remediation of toxic metal contaminated soils. J Hazard Mater 318:9–14
79. Xafenias N, Zhang Y, Banks CJ (2013) Enhanced performance of hexavalent chromium reducing cathodes in the presence of Shewanella oneidensis MR-1 and lactate. Environ Sci Technol 47:4512–4520
80. Singhvi P, Chhabra M (2013) Simultaneous chromium removal and power generation using algal biomass in a dual chambered salt bridge microbial fuel cell. J Bioremed Biodeg
81. Varia JC, Martinez SS, Velasquez-Orta S, Bull S (2014) Microbiological influence of metal ion electrodeposition: studies using graphite electrodes, [AuCl4] and Shewanella putrefaciens. Electrochimica Acta 115:344–351
82. Abourached C, Catal T, Liu H (2014) Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Res 51:228–233
83. Qiu R, Zhang B, Li J, Lv Q, Wang S, Gu Q (2017) Enhanced vanadium (V) reduction and bioelectricity generation in microbial fuel cells with biocathode. J Power Sour 359:379–383

84. Liu Y, Song P, Gai R, Yan C, Jiao Y, Yin D, Cai L, Zhang L (2019) Recovering platinum from wastewater by charring biofilm of microbial fuel cells (MFCs). J Saudi Chem Soc 23:338–345
85. Wang Z, Zhang B, Jiang Y, Li Y, He C (2018) Spontaneous thallium (I) oxidation with electricity generation in single-chamber microbial fuel cells. Appl Energy 209:33–42
86. Yaqoob AA, Ibrahim MNM, Rafatullah M, Chua YS, Ahmad A, Umar K (2020) recent advances in anodes for microbial fuel cells: an overview. Materials 13:2078
87. Zhang B, Feng C, Ni J, Zhang J, Huang W (2012) Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J Power Sour 204:34–39
88. Zhang B-G, Zhou S-G, Zhao H-Z, Shi C-H, Kong L-C, Sun J-J, Yang Y, Ni J-R (2010) Factors affecting the performance of microbial fuel cells for sulfide and vanadium (V) treatment. Bioprocess Biosyst Eng 33:187–194
89. Wang G, Huang L, Zhang Y (2008) Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotechnol Lett 30:1959
90. Huang L, Chen J, Quan X, Yang F (2010) Enhancement of hexavalent chromium reduction and electricity production from a biocathode microbial fuel cell. Bioprocess Biosyst Eng 33:937–945
91. Li Y, Lu A, Ding H, Jin S, Yan Y, Wang C, Zen C, Wang X (2009) Cr(VI) reduction at rutile-catalyzed cathode in microbial fuel cells. Electrochem Commun 11:1496–1499
92. Choi C, Cui Y (2012) Recovery of silver from wastewater coupled with power generation using a microbial fuel cell. Biores Technol 107:522–525
93. Tao H-C, Li W, Liang M, Xu N, Ni J-R, Wu W-M (2011) A membrane-free baffled microbial fuel cell for cathodic reduction of Cu(II) with electricity generation. Biores Technol 102:4774–4778
94. Ya-li F, Wei-da W, Xin-hua T, Hao-ran L, Zhuwei D, Zhi-chao Y, Yun-long D (2014) Isolation and characterization of an electrochemically active and cyanide-degrading bacterium isolated from a microbial fuel cell. RSC Adv 4:36458–36463
95. Choi C, Hu N (2013) The modeling of gold recovery from tetrachloroaurate wastewater using a microbial fuel cell. Biores Technol 133:589–598
96. Wang Y-H, Wang B-S, Pan B, Chen Q-Y, Yan W (2013) Electricity production from a bio-electrochemical cell for silver recovery in alkaline media. Appl Energy 112:1337–1341
97. Tandukar M, Tezel U, Pavlostathis SG (2009) Biological chromium (VI) reduction in microbial fuel cell: a three in one approach. Proc Water Environ Fed 2009:527–535
98. Huang L, Li T, Liu C, Quan X, Chen L, Wang A, Chen G (2013) Synergetic interactions improve cobalt leaching from lithium cobalt oxide in microbial fuel cells. Biores Technol 128:539–546
99. Wang Z, Lim B, Choi C (2011) Removal of Hg2+ as an electron acceptor coupled with power generation using a microbial fuel cell. Biores Technol 102:6304–6307
100. Tao H-C, Liang M, Li W, Zhang L-J, Ni J-R, Wu W-M (2011) Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. J Hazard Mater 189:186–192
101. Modin O, Wang X, Wu X, Rauch S, Fedje KK (2012) Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions. J Hazard Mater 235:291–297
102. Liu Y, Shen L, Song P, Chang D, Lu Z, Liu Y, Cai L, Zhang L (2019) Nickel (II) removal from wastewater by Microbial Fuel Cell. Int J Electrochem Sci 14:196–204
103. Sun M, Zhai L-F, Li W-W, Yu H-Q (2016) Harvest and utilization of chemical energy in wastes by microbial fuel cells. Chem Soc Rev 45:2847–2870
104. Li W-W, Yu H-Q, He Z (2014) Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. Energy Environ Sci 7:911–924
105. Kumar R, Singh L, Wahid ZA, Din MFM (2015) Exoelectrogens in microbial fuel cells toward bioelectricity generation: a review. Int J Energy Res 39:1048–1067
106. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337:686–690

107. Orellana R, Leavitt JJ, Comolli LR, Csencsits R, Janot N, Flanagan KA, Gray AS, Leang C, Izallalen M, Mester T (2013) U (VI) reduction by diverse outer surface c-type cytochromes of Geobacter sulfurreducens. Appl Environ Microbiol 79:6369–6374
108. Bermek H, Catal T, Akan SS, Ulutaş MS, Kumru M, Özgüven M, Liu H, Özçelik B, Akarsubaşı AT (2014) Olive mill wastewater treatment in single-chamber air-cathode microbial fuel cells. World J Microbiol Biotechnol 30:1177–1185
109. Singh HM, Pathak AK, Chopra K, Tyagi V, Anand S, Kothari R (2019) Microbial fuel cells: a sustainable solution for bioelectricity generation and wastewater treatment. Biofuels 10:11–31
110. Yaqoob AA, Ibrahim MNM, Yaakop AS (2021) Application of oil palm lignocellulosic derived material as an efficient anode to boost the toxic metal remediation trend and energy generation through microbial fuel cells. J Clean Prod, 128062
111. Yaqoob AA, Ibrahim MNM, Umar K, Bhawani SA, Khan A, Asiri AM, Khan MR, Azam M, AlAmmari AM (2021) Cellulose derived graphene/polyaniline nanocomposite anode for energy generation and bioremediation of toxic metals via benthic microbial fuel cells. Polymers 13:135
112. Jiang Y, Liang P, Zhang C, Bian Y, Yang X, Huang X, Girguis PR (2015) Enhancing the response of microbial fuel cell based toxicity sensors to Cu(II) with the applying of flow-through electrodes and controlled anode potentials. Biores Technol 190:367–372
113. Ahmad A, Siddique JA, Setapar SH, Lokhat D, Golandaj A, Ramjugernath D (2018) Recent advances in chitosan-based films for novel biosensor. In: Electrically conductive polymers and polymer composites: from synthesis to biomedical applications
114. Zhou M, Wang H, Hassett DJ, Gu T (2013) Recent advances in microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) for wastewater treatment, bioenergy and bioproducts. J Chem Technol Biotechnol 88:508–518
115. Yaqoob AA, Ibrahim MNM, Yaakop AS, Rafatullah M (2022) Utilization of biomass-derived electrodes: a journey toward the high performance of microbial fuel cells. App Water Sci 12:1–20
116. Dong Y, Qu Y, He W, Du Y, Liu J, Han X, Feng Y (2015) A 90-liter stackable baffled microbial fuel cell for brewery wastewater treatment based on energy self-sufficient mode. Biores Technol 195:66–72
117. Nancharaiah Y, Mohan SV, Lens P (2019) Removal and recovery of metals and nutrients from wastewater using bioelectrochemical systems. In: Microbial electrochemical technology. Elsevier, pp 693–720
118. Sivasankar P, Poongodi S, Seedevi P, Sivakumar M, Murugan T, Loganathan S (2019) Bioremediation of wastewater through a quorum sensing triggered MFC: a sustainable measure for waste to energy concept. J Environ Manag 237:84–93
119. Rahimnejad M, Bakeri G, Najafpour G, Ghasemi M, Oh S-E (2014) A review on the effect of proton exchange membranes in microbial fuel cells. Biofuel Res J 1:7–15

Application of Microbial Fuel Cells in Landfill Leachate Treatment

Irwan Ibrahim, Muhammad Farhan Hil Me, Mohd Nur Ikhmal Salehmin, and Swee Su Lim

Abstract The amount of waste produced each year is at an all-time high owing to high population expansion and urbanisation. Landfills have been and continue to be the most cost-effective waste disposal method. However, the environmental risks associated with leachate have caused surface and groundwater deterioration. As the leachate is hazardous, rich in organic, ammonia and metal elements, treating the liquid is energy-intensive and associated with costly procedures to fulfil current environmental laws. Microbial fuel cells (MFCs) could be the alternative method for leachate treatment. MFC is considered a promising and viable method because the device removes organic contaminants and generates bioelectricity during the oxidation process. This chapter investigates the robustness and effectiveness of the technology for removing carbon, nitrogen and phosphorus from landfill leachate and highlights and evaluates current developments in single and hybrid MFC. Recent advancements in combined MFC technology and their synergetic influence on boosting power densities, organic and nutrient removal and future difficulties were thoroughly explored. A sustainable strategy should be considered and designed for the MFC and its hybrid system to increase the success of the overall leachate treatment.

Keywords Microbial fuel cell · Landfill leachate · Wastewater treatment · Energy recovery · Organic carbon and ammonia removal

I. Ibrahim · M. F. Hil Me · M. N. I. Salehmin · S. S. Lim (✉)
Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
e-mail: limss@ukm.edu.my

I. Ibrahim
e-mail: p112458@siswa.ukm.edu.my

M. F. Hil Me
e-mail: p94598@siswa.ukm.edu.my

M. N. I. Salehmin
e-mail: ikhmal@ukm.edu.my

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_16

1 Introduction

1.1 Leachate Characteristic

Leachate production is a significant issue for municipal solid waste (MSW) landfills, posing a severe hazard to surface and groundwater. Leachate is a liquid that has extracted dissolved and suspended debris from a landfill as it travels through it. Leachate is produced by precipitation entering the landfill due to moisture in the garbage as it decomposes. Landfill leachate is multi-contaminant wastewater with high amounts of organic materials. The chemical oxygen demand (COD) and biochemical oxygen demand of certain leachates (BOD_5) can go up to 60,000 and 30,000 mg/L, respectively, with the ammoniacal nitrogen compounds estimated up to 2,000 mg/L, and hazardous metals in various concentrations [1]. The pollutant strength of leachate is 100 times that of municipal wastewater [2]. Organic and inorganic debris, high amounts of ammonia nitrogen, phosphate, phenols, toxic metals, sulphide, dissolved salts, xenobiotic organic compounds and microbes are all found in landfill leachate, which has a black appearance [3–5]. The contents of leachates are complexes and dynamically change in relations to the spatial and temporal variations. Various factors can contribute to the composition changes including local climate, landfill age, waste types, waste site conditions, surface water distribution and movement, landfill architectures and operation arrangement [4, 6–9]. In order to classify and generalise the landfill leachate, age of the landfill site is the key element to determine its physical, chemical and biological features. It has been used as a reference point for leachate categorisation which can be further divided into three types depending on its age. Table 1 indicates the characteristic of the juvenile, intermediate and mature leachates [4, 10, 11].

Table 1 Classification of the landfill leachate according to its characteristic

Parameter	Young (<5 year)	Intermediate (5–10 years)	Mature (>10 years)
COD	>10,000	4,000–10,000	>4,000
BOD_5/COD	>0.3	0.1–0.3	<0.1
pH	6.5	6.5–7.5	>7.5
Organic content	80% VFA	5–30% VFA + humic and fulvic acids	Humic and fulvic acids
Heavy metals	Low-medium	Low	Low
Biodegradability	High	Medium	Low

1.2 Leachate Treatment Process

Several leachate management systems and treatment technologies have arisen and have been used for leachate treatment in recent decades. As illustrated in Fig. 1, comprehensive treatment of various kinds of landfill leachates (i.e. from young to mature) has been achieved by combining diverse treatment procedures, including physical, chemical and biological processes [4, 12, 13].

Leachate was blended with residential wastewater before cotreatment in the wastewater treatment plant to improve biodegradability and BOD/COD ratios [14, 15]. Landfill leachate (20% v/v) was introduced to a wastewater treatment plant that employed a sequential batch reactor. The amount of ammonia, nitrite, COD and turbidity were 93, 83, 70 and 83% eliminated, respectively, after a 6-day hydraulic retention time [15]. Mojiri et al. [14] pointed out that comparing landfill leachate treatments to methods used for household wastewater is problematic due to high COD and BOD. To treat leachate, a combination system should be used. Li et al. (2017) used denitrification/nitrification or partial nitrification (anammox) to remove nitrogen from intermediate landfill leachate. The maximum total nitrogen (TN) removal rate and TN elimination efficacy were 0.45 m^3/d and 96.7%, respectively. The denitrification/nitrification process allows an increase in BOD in wastewater, which allows for nitrate removal, and an increase in autotrophic bacteria growth.

According to [16], adsorption has been widely used to treat landfill leachate. There are a few advantages such as easier to use, simpler design, robustness and ability to remove various contaminants are advantages of this technology [17]. However, the process increases the cost of the treatment as the active materials required replacement and regeneration from time to time. Pollutants can cling to the surface of the adsorbent in a variety of ways during adsorption (Fig. 2). The adsorbent's surface has special properties that allow the adsorbate to stick to it. Adsorption occurs under particular conditions, and desorption, a reversible event, is applicable. Adsorbates can

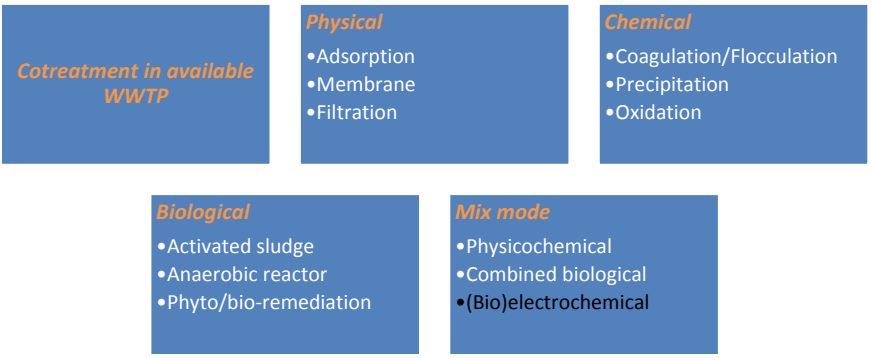

Fig. 1 Conventional leachate treatment methods

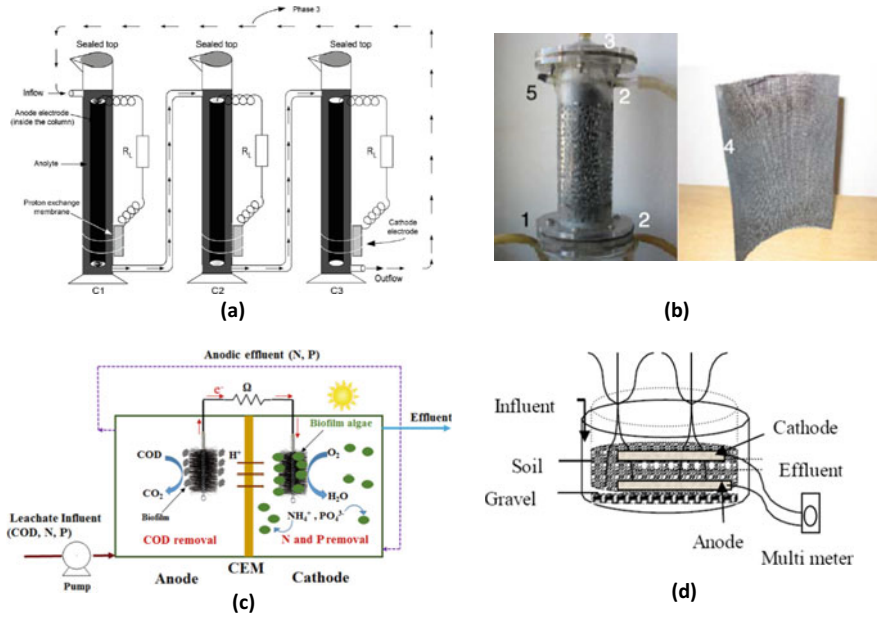

Fig. 2 Unconventional MFC for improved leachate treatment: **a** multistage series column, **b** upflow open-air membraneless reactor, **c** algae-assisted MFC and **d** evapotranspiration plant MFC

be liberated from the adsorbent's surface and returned to the liquid during desorption (Bello & Raman). The utilisation of various membrane technologies to treat wastewater has gotten a lot of attention [18]. Membrane selects and filters influent via different-sized holes [19]. The primary membrane technologies used in landfill leachate treatment are microfiltration, dynamic membranes, nanofiltration, ultrafiltration and reverse osmosis [18]. Membranes provide a number of advantages including low energy consumption, simpler and effective [20]. Coagulation, in its most basic form, allows small particles (colloids) in wastewater to destabilise and form a floc that may be easily settled [21]. The efficacy of coagulation/flocculation is determined by the coagulants/flocculants used. Aluminium sulphate, polyaluminium chloride and ferric chloride are common trivalent-metal inorganic salts used as coagulants [22]. According to [23], the main advantage of this treatment is its excellent efficacy in eliminating organic debris, suspended particles and humic acids. The cost of chemicals and the handling of created sludge are, however, disadvantages. Fenton, ultraviolet, ozonation and electrochemical oxidation reaction use a mix of oxidants and catalysts to create hydroxyl radicals (·OH) in solutions that is able to degrade hazardous compounds in wastewater [24]. The most significant disadvantage of advanced oxidation processes is their high capital and operating costs. The microorganism's metabolic activities result in the biological breakdown of pollutants. Biological approaches are often employed to remove nutrients or organic compounds such as ammonia and fatty acids due to their cost-effectiveness; nevertheless, such

techniques may not be effective on heavy metal removal due to the characteristics of the nonbiodegradable organics [25]. Dabaghian et al. [18] classify biological technologies into aerobic and anaerobic biological procedures. In phytoremediation procedures, to break down and inactivate potentially hazardous components [26]. Phytoremediation has a number of advantages, including 1 minimal installation and energy costs. Meanwhile, bioremediation uses algae including microalgae, various fungi and bacteria for local landfill leachate treatment. It is considered a cost-effective and environmentally friendly solution. Several physicochemical treatment technologies have been combined to improve removal efficiency and reduce energy usage in leachate treatment. Fedorov et al. [27] suggested that hybrid procedures, particularly in advanced oxidation processes, with other treatments could save energy. There have been four integrated systems identified for combined physicochemical approaches, with (i) membranes, (ii) coagulation (iii) adsorption and (iv) membrane separation and filtration combined with coagulation or adsorption. Landfill leachate is routinely treated using biological methods. However [28], found that a biological method alone is insufficient to remove most of the refractory pollutants from landfill leachate. As a result, researchers [14] have proposed using a combination of biological and physicochemical strategies to improve biodegradability ratios and biological performance in landfill leachate treatment. Five frequent combination treatment strategies have been found. The integration of the biological treatment with (i) adsorption, (ii) oxidation, (iii) membrane, (iv) coagulation and (v) constructed wetlands. Bioelectrochemical systems (BES) have been developed in recent decades. The purpose of the system is aimed for waste treatment and energy recovery. They are characterised as a mix of biological and electrochemical technologies for generating power and removing contaminants from various substrates [29–32]. BES is often based on the microbial interaction at the electrode surface, which exchanges electrons with solid electrodes to remove contaminants [33–36]. Microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and microbial desalination cells (MDCs) are the most common system among the technologies used in BES [37], with MFCs being the most commonly used for landfill leachate treatment in recent years. MFC consists of an anode and cathode compartments separated by an ion-selective membrane [38–42]. Organic substrates are oxidised at the anode compartment anaerobically by an electrochemically active microbe in MFC. This process generates electrons and protons, which are transferred to the cathode directly (electroactive bacteria) or indirectly (mediators) [43–45]. These electrons and protons are then used at the cathode by reducing oxygen to water, producing bioelectricity via external circuit. The difference in redox potential between the cathode and anode provides the driving force behind the entire process [43, 44]. Compared to aerobic activated sludge, MFC produces 2.4–26.5 times less sludge as mentioned by Chen et al. [6].

2 Leachates as Promising Substrate for MFCs

Landfill leachates are regarded as valuable substrates for MFCs due to their organic rich contents. MFC leachate treatment is considered one of the cutting-edge and environmentally friendly treatment techniques in the modern world. Additional benefits from the treatment include bioelectricity generation and excellent discharge quality [45–48]. Several MFC configurations used in landfill leachate have been explored consisting of single-, double-chamber, upflow and stacked designs. The main purpose is to increase electricity production and organic removal. As leachates are organic and inorganic rich substances, treating them could be an energy and cost-intensive process. In this chapter, we will first look into the performance of various standalone MFC designs and understand the concept of specific medication that benefit the leachate treatment. Further investigation involves the combination of MFC with other processes that focus on carbon and nitrogen removal, phosphorus recovery and simultaneous power production. The composition of landfill leachate, as well as other characteristic parameters such as pH, electrode material, temperature and configuration, have a considerable impact on MFC treatment [44, 49–52]. One of the main issues is the electricity production from leachate is often minimal in MFC because the leachate substrate is less biodegradable (complex ammonia and nitrogen compounds) and consists of inorganic matters (hazardous metals) [48, 53, 54]. Nonetheless, the electricity generated may not be able to offset some of the energy used during the treatment.

3 Recent Advances on MFCs Treating Leachates

3.1 Conventional Single- and Dual-Chamber MFCs

A single-chamber MFC (SCMFC) consists of a single chamber where the anode and cathode electrodes are located in the same compartment. With various types of air cathode, the cathode is normally an open-air electrode [55–59]. Despite single-chamber MFCs' cheaper cost and simplicity, most landfill leachate treatment studies focused on power production and organics removal, with a small number of researchers monitoring ammonia and nitrogen removals. The design and operating requirements of SCMFCs for landfill leachate treatment, such as electrode material and surface area, inoculation procedure, and separator, all affect power densities. When using a Zirfon membrane with real leachate and an up-flow air cathode membrane-MFC to remove COD, the removal effectiveness varied from 7 to 89% [60, 61]. Furthermore, the energy generated by SCMFC was between 70 and 20,0 0 mW/m^3 as volumetric power density and the Coulombic efficiency was between 1 and 80% [49, 57, 61, 62]. The most investigated electrode materials in SCMFCs were found to be carbon-based compounds. Despite this, there was a significant disparity in power density and organic removal efficiency, which might be attributed to variable

operating conditions in each experiment. According to Hernandez-Flores et al. [49], the power produced by an air cathode SCMFC fed with young leachate and fitted with a proton exchange (agar-based) membrane (20,000 mW m^{-3}) was three times greater than that of a Nafion 117 membrane (6,800 mW m^{-3}). The accumulation of dry salts on the exterior side of the cathode electrode and the higher pH of the influent stimulated the movement of cations rather than protons with Nafion membranes. However, as compared to Nafion membranes, the MFC with the low-cost membrane obtained better organic removals of 39.32%. Apart from the designs and configurations, the influent leachate type is an essential element in MFC, since it affects the treatment and bioelectricity production. Regarding bioelectricity production and organic removal performance, Hernández-Flores et al. [59] assessed the air cathode SCMFC fed with municipal wastewater and a combination of municipal wastewater and landfill leachate. The Coulombic efficiency was recorded at 47.5% and the COD removal efficiency was 80% for municipal wastewater. Slight increases in COD removal (86%) for the combined municipal wastewater and landfill leachate. MFC fed with leachate substrate had a maximum power density of 489 mW m^{-3}, which was greater than those fed with municipal wastewater (315 mW m^{-3}) or combined municipal wastewater and landfill leachate (82 mW m^{-3}). This might be attributed to the landfill leachate substrate's increased electrical conductivity and organic content. In the latter study, Hernandez-Flores et al. (2017b) compared the power density and organic removals of SCMFCs fed with three different substrate mixing ratios of landfill leachate/sulphate reducing inocula (Mixture 1: 30% LFL/70% SR–I, Mixture 2: 70% LFL/30% SR–I, and Mixture 3: 50% LFL/50%t SR-I). Mixture 2 (8050 mW m^{-3}) and Mixture 3 (4260 mW m^{-3}) were found to have greater power density (10,380 mW m^{-3}) than SCMFC with Zirfon membrane with 50% LFL/50% SR-I. COD removals were greater in SCMFCs equipped with Nafion membrane in Mixture 1 than in Mixture 2 and Mixture 3. The average COD removals of Mixture 1, Mixture 2 and Mixture 3 were 68.42%, 64% and 48.11%, respectively. The findings demonstrated the critical importance of choosing the optimal membrane type and influencing substrate compositions for obtaining maximum power generation.

3.2 Unconventional Type MFCs

MFC has been reinvented from the single and dual chamber to specific configurations to improve landfill leachate treatment and electricity generation. The new configurations include the multistage column, up-flow air cathode, algae-assisted, and evapotranspiration-MFC which are discussed in this section.

One of the common designs is the multiple-stage column MFC to increase leachate treatability [63]. The MFCs were connected in series, with a single feed line into the first and then the second column and outflow from the third final column. It also investigated how the increases of electrode surface area affected columns' performance. The electrode surface area increased from 360 to 1080 cm^2 actually improving the power output by 2–3 folds in the MFCs. The hydraulic retention time (HRT) was

further increased by recycling the third column's outflow into the first column's feed line. In the recycle mode, the COD and BOD removals were increased up to 79 and 82% after 4 days of operation.

Unlike the multistage column MFC, up-flow air cathode membrane-free MFC has a simpler design with an inlet from the bottom of the reactor [60]. The Pt-coated cathode was bonded into the outside wall of the anode tube to reduce charge resistance and increase air surface coverage. The MFC could constantly produce 0.6 mW power from leachate during the 50 h operation duration. The maximum achievable volumetric power and current were 12.8 W m^{-3} and 41 A m^{-3}. The total Coulombic efficiency (CE) decreased from 14.4 to 1.2% when the organic loading rate was increased from 0.65 to 5.2 kg COD m^{-3} day^{-1}. The poor CE may be due to the open-to-air cathode's severe oxygen diffusion.

Another unconventional type of MFC is the algae-cathode MFC. Landfill leachate was first treated in anode to remove organic carbons. Algae was used to assist the cathode reaction and further treat the leachate effluent from the anode to remove the remaining ammonium and phosphorus [64]. Diluted landfill leachate (15% v/v) was treated in the anode chamber with varying hydraulic retention durations (HRTs). The HRT significantly impacted the cell voltage and dissolved oxygen (DO) in the cathode. The greatest cell voltage was 303 mV after 20 h of HRT, while the highest DO concentration was 5.3 mg/L at 60 h of HRT. The greatest removal efficiency for ammonium and phosphorus was 76.4% and 86.3%, respectively, with 60 h of HRT. At 60 h of HRT, the maximum COD elimination of 26% was recorded. Zaman and Wisnu Wardhana [65] use evapotranspiration-MFC for the first time to treat leachate. Evapotranspiration uses natural evaporation process and bacterial activity on plant roots and plant medium to remove organic matters in wastewater. Two native flora, *Alocasia macrorrhiza* and *Eleusine Indica* were cultivated separately in a horizontal MFC, with the cathodes and anodes in separate chambers (i.e. in the leachate reactor and reactor with plant media). The electric power produced by *Alocasia macrorrhiza* plant MFC was 70 watts, while the *Eleusine Indica* grass was 60 watts during the 30 days of reactor operation. The author demonstrated that the evapotranspiration-MFC could be one of the promising systems for leachate treatment and electricity generation. However, further detailed investigation was required to prove the concept.

3.3 Hybrid System

With the growing age of mature leachate, the proportions of resistant and complex nitrogen compounds will predominate, making a single-step MFC treatment impractical [66]. Tables 2 and 3 indicate how a varying percentage of landfill leachate (from young to mature) has been utilised as fuel in standalone MFCs. Poor current densities and removal efficiency, especially nutrient removal using solo MFCs, motivated researchers to look for new ways to solve these problems. As a result, combining MFCs with other technologies was workable, feasible and led to improved efficiency

Table 2 Leachate treatment via MFCs

Electrode material	Operational mode	Leachate		COD removal	NH_4^+–N removal	CE	P_{max} (mW/m^3)	Refs.
Single chamber MFC								
Granular graphite/$Ru_xMo_ySe_z$	Batch	Real	<5 years	71	–	77	13,746	Vázquez-Larios et al. [57]
Graphite flakes/carbon cloth	Batch	Real	<5 years	39.3	–	71.7	20,000	Hernández-Flores et al. [49]
Carbon paper/carbon cloth	Batch	Real	<5 years	69.5	–	6.6	6817	Zhang et al. [60]
Carbon cloth	Continuous	Real	<5 years	89.4	23.3	14.4	12,800	You et al. [74]
Dual chamber MFC								
Carbon felt	Batch	Synthetic	>10 years	65.1	33.2	–	135 mW/m^2	Huang et al. [75]
Carbon black	Continuous	Real	–	–	92.8	–	0.4mW	Alabiad et al. [76]
Carbon cloth	Batch	Simulated	>10 years	90	–	19.7	230 mW/m^2	Li and Chen [77]
Carbon felt	Batch	Real	<5 years	90	59.1	21.3	98.6 mW/m^2	Hassan et al. [48]
Graphite sheets	–	Real	–	100	–	–	9150	Kumar et al. [78]

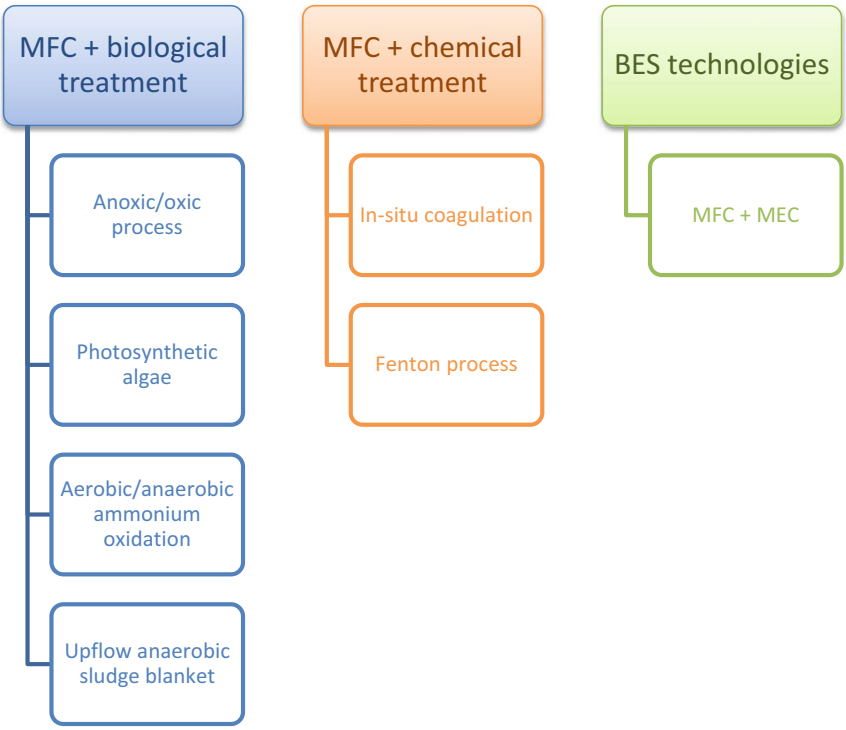

Fig. 3 Combined MFC with other treatment processes

and robustness [67–69]. Coupled systems' final effluents may comply with environmental standard regulation with socio-economic advantages over solo systems. As illustrated in Fig. 3, these combinations were categorised based on two basic processes: biological and chemical. Due to its potential to improve nutrient removal and ease of installation with current biological technologies, biological combinations are more frequent with MFC than chemical and physical processes. A plethora of biological combinations have been developed for landfill leachate treatment using MFC and biological processes, including up-flow anaerobic sludge blanket, anaerobic ammonium oxidation (Anammox), aerobic ammonium oxidation, biological anoxic/oxic and photosynthetic with algae bacteria. Because of its high nutrient removal and simplicity of installation with current biological technologies, MFC in conjunction with other biological processes, such as anoxic/oxic processes, is most widely used [70–73].

MFC with anoxic/oxic process. Nitrification and denitrification occurred by the metabolisms of aerobic autotrophic and anoxic heterotrophic bacteria, respectively. Ammonia is converted to nitrate (nitrification) and subsequently reduced to nitrogen

gas (denitrification) in the anoxic/oxic processes. Design and operational characteristics such as solid or hydraulic retention time (SRT or HRT), temperature, recirculation rate, pH and loading rate affect the biological processes. Additional work to determine the best-operating conditions for high-treatment quality and bioelectricity production is required to integrate the MFC with the anoxic/oxic process. Zhang et al. [71–73] in their previous studies investigated this system for effective landfill leachate treatment. The anoxic/oxic process can be combined with MFC in the cathodic chamber to achieve larger nitrogen reductions and at a lower energy cost via sequential intermittent aeration mode. Zhang et al. (2015b) manipulated the organic loading rate, organic and ammonia removal in a recirculation membrane-less MFC. At an OLR of 3 kg COD m^3 day^{-1}, the greatest power densities of 2.71 w/m^3 were found, which thereafter decreased to the lowest (0.36 w/m^3) as the OLR increased to 4.2 kg COD m^3 day^{-1}. While the highest COD (95.1%) and ammonia (99.9%) reductions were achieved with the lowest loading rate of 1.2 kg COD m^3 day^{-1}. The acquired power density (2.85 w/m^3) was greater than the earlier results at the same OLR of 3 kg COD m^3 day^{-1} when the system was operated with intermittent aeration, 24 h as HRT and 3 kg COD as OLR. In addition, the effluent dissolved organic matter was detected in combination with the COD and ammonia reductions in the same cathodic chamber. The organic matters were decomposed faster in the anoxic/oxic MFC cathodic chamber than the traditional anoxic/oxic reactor resulting in more COD and ammonia removal. In the MFC chamber, 86.3% of COD and 96.7% of NH_4^+–N were removed, which was much greater than the traditional reactors, which only removed 11% and 47% of COD and NH_4^+–N, respectively [73]. Khan et al. [70] demonstrated wastewater treatment including biorecalcitrant phenol and 2,4,6-trichlorophenol in dual-chamber MFC under anoxic and oxic conditions, similar to landfill leachate. In the cathode chamber, coated anodic electrodes with polyaniline (PANI)/SnO_2 and oxic treatment conditions provided outstanding power output. The addition of PANI/SnO_2 to a plain carbon cloth electrode increased the surface area and electrical conductivity, resulting in better system performance and power density. The highest power density in the oxic state was 522.77 mW/m^2, which was significantly higher than the 454.81 mW/m^2 in the anoxic condition. COD removals were also enhanced in the presence of modified anode electrode in oxic circumstances, with 85.58 and 82.67% removals, respectively, for oxic and anoxic conditions.

MFC with photosynthetic algae. Algae can grow quickly in a variety of environments, capture CO_2 to decrease greenhouse gas emissions and recover biomass resources. A cathode made of algae may absorb light and convert it into bioenergy that can be used to make sustainable and environmentally friendly value-added biofuels. MFC combination with algae is accompanied by in situ oxygen production in the cathode chamber rather than relying on an input air supply to improve power densities and nutrient removal [79–81]. In the past few years, the integration of MFC with algae has been widely explored in wastewater treatment [82–85], while a few studies on landfill leachate have been published in literature. Researchers have shown that algae may be used as a cathode in MFCs, providing an energy transfer background in combination with accumulated value products in algal biomass. It also

energetically increases energy recovery and removes pollutants from the algal MFC cathode. Many efforts have been made to mitigate the impact of greater quantities of organic matter and ammonia nitrogen in landfill leachate, while at the same time recover the latent energy. Different concentrations (5, 10, 15, 25 and 40%) of landfill leachate were combined with household sewage containing algae and utilised as catholyte in MFC-Algae as studied by Nguyen et al. [68]. The fractional concentrations were tested in order to determine the best mixing ratio for ammonia and COD removal as well as energy recovery. At 5% leachate, the largest nutrient removal efficiency (97.3% as NH^{4+}) and highest cell voltage (300 mV) were recorded, compared to other concentrations (10, 20, 25 and 40%). Lower ammonia removals might be due to high ammonia concentrations at high leachate fraction ratios. The maximum COD removal effectiveness (52%) was recorded at 10% leachate fractions in the algae-based MFCs.

MFC with aerobic/anaerobic ammonium oxidation. The Anammox process is a type of anaerobic ammonium oxidation performed by autotrophic anaerobic ammonium oxidation bacteria. During the anammox process, ammonium is partially oxidised to nitrite in anaerobic or anoxic conditions without the need for a carbon source. The accumulated nitrite serves as an electron acceptor and is reduced to nitrogen gas [86–91]. The carbon and nitrogen fractions in leachate will be utilised in different metabolic reactions; to generate electricity in MFC and served as an electron acceptor for anaerobic ammonium oxidizing bacteria, respectively. The unique targeting mechanisms make the MFC a perfect pretreatment unit for organic carbon and nitrogen removal with a surplus electricity generated from the process. Anammox is an anaerobic process that may be halted by high levels of dissolved oxygen in leachates. The key operational factors that may impact the process efficiency are hydraulic retention time (HRT), temperature and pH. The synergetic collaboration between the MFC and the anammox process has shown excellent results in terms of nitrogen removal, power density and cost reduction without the addition of carbon source for ammonia and nitrogen removal. Lee et al. [69] compared the energy production and ammonia removals in two different MFC hybrid systems, namely ammonium oxidation/MFC and MFC/Anammox. MFC/Anammox produced nearly 50% more energy than Ammonium oxidation/MFC. During the ammonia oxidation/MFC process, ammonia was aerobically transformed to nitrate in a separate reactor and then nitrate was converted to nitrogen gas in the MFC reactor's subsequent cathode chamber (nitrate pathway). Organic compounds in landfill leachate were used in the anode chamber, while ammonia was removed in the cathode chamber by oxidising to nitrite and subsequently reduced to nitrogen gas via Anammox nitrite pathway. The output power density and ammonia removals in the MFC/Anammox process were higher than those in ammonium oxidation/MFC process, with averages of 12 mW/m^2 and 94% TN in MFC/Anammox and 8 mW/m^2 and 92% TN in MFC/Anammox and ammonium oxidation/MFC, respectively, due to the contribution of organic matter decomposition in MFC.

MFC with anaerobic digestion. Because of its stability combined with energy production and resource recovery, anaerobic digestion process has been widely applied for various types of liquid and solid-state pollutants during the previous

century. Anaerobic digestion was also used for treating substrates with a high organic strength and resistant chemicals such as industrial waste, food processing wastewater, landfill leachate and biorefinery wastewater [4, 92]. One of the greatest examples is the up-flow anaerobic sludge blanket (UASB) process developed for anaerobic treatments that are able to achieve high effluent quality at low HRT and high OLR. Nevertheless, the performance is heavily dependent on temperature changes and presenCw of toxic substances, thus further treatment is required to ensure the final effluent quality [4, 92]. As a result, following UASB, an electrochemical process like MFC may be utilised as a polishing treatment method and complies with strict environmental laws. Tugtas et al. [93] assessed the power generation, organic and ammonia removal efficiency of a DCMFC fed with anaerobically prepared landfill leachate (effluent of a UASB) in batch and continuous operating modes, with HRT ranging from 15 days. The maximum power density was obtained in continuous operation mode with increasing HRT from 1 to 5 days, with an average of 158 mW/m^2 (2482 mW/m^3), while in batch mode only 109 mW/m^2 (1712 $mW/^3$) was obtained, which could be due to partial nitrification occurring when the HRT was increased.

MFC with coagulation. Coagulation and electrocoagulation-based chemical treatment processes were widely used in previous research [94] and attracted great attention for landfill leachate treatment including biorefractory organic materials. The integration of biological therapy and the coagulation process was investigated and the treatment of leachate was enhanced [95, 96]. Kumar et al. [97] looked at the impact of solo coagulants and MFC-coagulation processes on landfill leachate treatment and electricity generation. Only 78.6% of COD was eliminated by a pH 8 coagulation procedure, but MFC combined with anodic coagulation together removed more than 98.7% of total COD after 3 days. In addition, the integration of MFC with in situ production of anodic coagulants yielded a volumetric power density of 6644.6 mW/m^3 and demonstrated a lucrative and feasible treatment procedure for a variety of landfill leachate treatment applications.

MFC with Fenton process. Many resistant compounds, notably poor biodegradability wastewater and mature landfill leachate, have been successfully degraded using Fenton-based electrochemical advanced oxidation techniques. Toxic chemicals in landfill leachate may be oxidised by Fenton's reaction (H_2O_2/Fe^{2+}) to hydroxyl radicals [98–101]. The primary disadvantage of the chemical Fenton process is its higher operating costs owing to external H_2O_2 addition. However, MFCs can only decompose organic contaminants with poor removal effectiveness towards refractory organics. As a result of the in situ creation of H_2O_2 from MFC reactions, the power demands for Fenton reactions might be met via MFC reactions, while greater pollutant removals can be accomplished [102]. The integrated MFC-electro-Fenton process has recently been widely researched in wastewater treatment [98, 99, 101, 103, 104]. With anammox pretreated landfill leachate, Hassan et al. [99] investigated DCMFC-based bio-electro-Fenton process organic removal efficiency and output current density. With iron (Fe^{2+}) sulphate and iron (Fe^{3+}) chloride additions at 150, 300, and 500 mg/L as Fenton catalyst, the effluent of Anammox process was studied. Anodic chambers with synthetic anolyte (glucose) had greater COD removals (71–76%) than those with 100% landfill leachate (lower COD removal).

The maximum COD removal efficiency of 34.6, 1.7, 40.7 and 3.1% were obtained with real LFL and at 300 mg/L iron (Fe^{2+}) sulphate, and the removals decreased to (31.4, 12.2, 35.2, 13.8) by using the same dosage of iron (Fe^{3+}) chloride. However, the output current density in synthetic or actual landfill leachate was between 600 and 700 mA/m^2. Hassan et al. [98] employed Anammox pretreated landfill leachate as MFC electro-Fenton substrate. Various electrode materials and operating modes (batch and continuous) have been reported to achieve COD reductions of 35–65% and CE removals of 22–29%. The pH stress on anodic electrogens caused by recirculating acidic catholyte to anode chamber was shown to reduce anode performance. The effectiveness of COD removals and CE was not great in earlier publications, especially in cathodic chambers, therefore additional study is required. Recent research by Wang and coworkers [105] investigated the refractory organics degradation of real landfill leachate in an integrated bio-electro-Fenton process using single-chamber air cathode MFC and DCMFC with three different cathode materials: nano-zerovalent iron and modified activated carbon (nZVI@MAC), nano-zerovalent iron and activated carbon (nZVI@AC) and Activated Carbon (AC) (AC). SCMFC at nZVI@MAC was able to produce highest power density (935 mW/m^2) and average COD removal efficiency (79%) over nZVI@AC and AC. The superior 2e ORR in MAC than AC and nZVI@AC cathode is attributed to the greater performance of nZVI@MAC.

MFC with MEC. The presence of carbon source molecules and ammonical nitrogen ions in leachates might stymie the traditional nitrification and denitrification processes [106]. In high-strength wastewater and landfill leachate, the anaerobic treatment procedure has proved to be successful. However, low temperatures and inappropriate feed source compositions (low C/N) might restrict methane generation in anaerobic digestion [107, 108]. H_2 gas has recently gained popularity as a renewable energy source as it is an excellent energy carrier that is both clean and environmentally beneficial. Biohydrogen recovery through micro-bial electrolysis cells (MECs) is a viable method for landfill leachate remediation in terms of sustainability and economics by generating side by-product for commercilisation [109, 110]. Furthermore, enhanced leachate conductivity and buffering capacity might improve process stability and biohydrogen generation [67]. Anodic electrogenic bacteria are utilised in MECs to decompose organic materials, resulting in protons and electrons that may be transmitted to the cathode chamber through the electrolyte circuit and reduced to H_2 gas in the absence of O_2. The redox potential processes are constantly directed by the external potential (0.5–1.0 V) in MEC [48]. By connecting MFC with MECs in sequence, several efforts have been made to eliminate the energy necessary for H_2 synthesis [111]. In terms of COD, the coupled MFC–MEC process outperformed the single MFC by roughly 268%. Zhang et al. [102] recently published promising research in which a series of MFCs were combined with an ammonia electrolysis cell (AEC) with nano-Mo_2 C modified glassy carbon (GC) cathode electrodes. When fed with a glucose and ammonium mixure, the power density and H_2 production rate were 536 mW/m^2 and 59 L/g Mo_2 C/N-rGO h^{-1}, respectively. When the diluted landfill leachate (1:4) was used as a substrate, the output power density and H_2 productivity were 143 mW/m^2 and 42 L/g Mo_2 C/N-rGO h^{-1}, respectively. Surprisingly, the linked system was able to remove 70.7% more ammonia,

with the stacked MFC contributing 23.2% and the AEC 47.5%. Zhou et al. [112] employed Mo_2 C/NGA modified glassy carbon (GC) cathode electrodes to increase the hydrogen evolution reaction activity in linked MFC–AEC. When diluted landfill leachates were employed, the H_2 productivity rate was enhanced to 79.2 L/g Mo_2 C/NGA.

4 Conclusion and Future Perspectives

MFC has developed as a potential eco-friendly treatment technique for a wide range of substrates in the past two decades. The potential of the MFC have been drawing researcher attention to use the technique in landfill leachate treatment. In this chapter, the MFC-based treatment methods and their configuration combined with other techniques found in literatures have been briefly summarised. MFCs have shown their viability in organic and ammonia removal, however, their scalability is limited due to lower power densities and expensive construction costs. To increase MFC efficiency and maximise electricity production, a number of different measurements can be used. This includes the selection of low-cost materials and optimisation of operational conditions. Apart from that, a combined system (MFC and other treatment processes) could significantly reduce the operational cost and increase treatment efficiency compared to the single MFC process. More work is still required to investigate and improve methodologies in MFCs, especially on site leachate treatment as it might vary according to the weather and local condition. Designing and developing a process involve the reuse and recycle of the wastes like landfill leachate become the key components of the modern world targets, especially under the United Nations for Sustainable Development Goals (UN-SDGs). It also results in increasing people's attention to circular economy rather than merely recovering the energy or materials in order to preserve their practical worth. High-contaminated wastewater leaches from the degradation of solid wastes at the landfill sites could cause damage to local environment and create a formidable threat to ecosystem. MFC provides alternative solutions to leachate treatment, metal and energy recovery in the same device. It has been proven in the studies mentioned above that bioelectrochemical technologies can be effectively treated leachate while generating electricity and/or producing valuable products such as metals and compost to offset the operation cost. Figure 4 shows the leachate sustainability in conjunction with treatment process. Up to date, there is still less information regarding on site implementation of the MFC-based system and the function of reducing the leachate contamination before it disperses to nearby environment and further contaminates groundwater. Future planning would be focused on the implementation of the MFC-based system at the landfill site by considering the treatment sustainability that can tackle the leachate, return the treated water to environment, recovered metals and composting for reuse and recycle purposes.

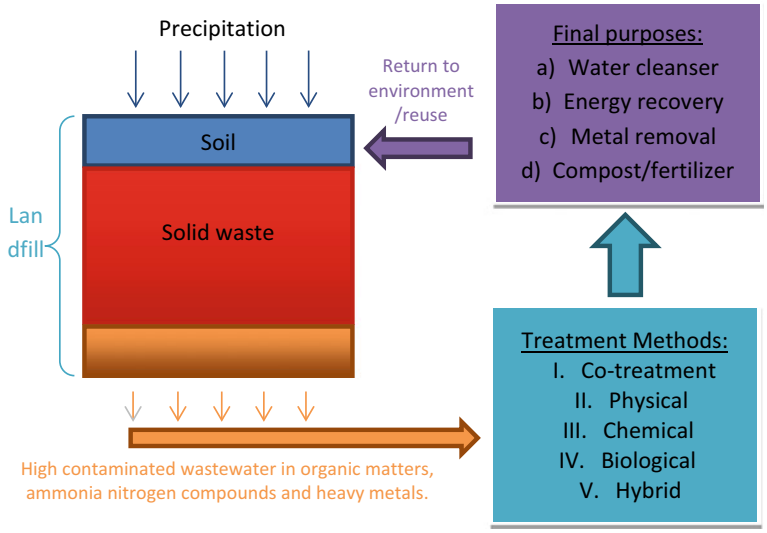

Fig. 4 Overview of landfill leachate formation, treatment process and final usages in eliminating waste and pollution

References

1. Aziz H, Hosseini M (2012) Solid waste disposal by semi-aerobic sanitary landfill: towards achieving a sustainable development (penang experience)
2. Koshy L, Paris E, Ling S, Jones T, BéruBé K (2007) Bioreactivity of leachate from municipal solid waste landfills—Assessment of toxicity. Sci Tot Environ 384(1):171–181. https://doi.org/10.1016/j.scitotenv.2007.06.017
3. Eggen T, Moeder M, Arukwe A (2010) Municipal landfill leachates: A significant source for new and emerging pollutants. Sci Total Environ 408(21):5147–5157. https://doi.org/10.1016/j.scitotenv.2010.07.049
4. Renou S, Givaudan J, Poulain S, Dirassouyan F, Moulin P (2008) Landfill leachate treatment: review and opportunity. J Hazard Mater 150(3):468–493. https://doi.org/10.1016/j.jhazmat.2007.09.077
5. Zhang H, Li Y, Wu X, Zhang Y, Zhang D (2010) Application of response surface methodology to the treatment landfill leachate in a three-dimensional electrochemical reactor. Waste Manag 30(11):2096–2102. https://doi.org/10.1016/j.wasman.2010.04.029
6. Chen W, Zhang A, Gu Z, Li Q (2018) Enhanced degradation of refractory organics in concentrated landfill leachate by Fe0/H_2O_2 coupled with microwave irradiation. Chem Eng J 354:680–691. https://doi.org/10.1016/j.cej.2018.08.012
7. Fernandes A, Pacheco M, Ciríaco L, Lopes A (2015) Review on the electrochemical processes for the treatment of sanitary landfill leachates: present and future. Appl Catal B 176–177:183–200. https://doi.org/10.1016/j.apcatb.2015.03.052
8. Kjeldsen P, Barlaz MA, Rooker AP, Baun A, Ledin A, Christensen TH (2002) Present and long-term composition of MSW landfill leachate: a review. Crit Rev Environ Sci Technol 32(4):297–336. https://doi.org/10.1080/10643380290813462
9. Shehzad A, Bashir MJ, Sethupathi S, Lim JW (2015) An overview of heavily polluted landfill leachate treatment using food waste as an alternative and renewable source of activated carbon. Process Saf Environ Prot 98:309–318. https://doi.org/10.1016/j.psep.2015.09.005

10. Ahmed FN, Lan CQ (2012) Treatment of landfill leachate using membrane bioreactors: a review. Desalination 287:41–54. https://doi.org/10.1016/j.desal.2011.12.012
11. Hassan SH, van Ginkel SW, Hussein MA, Abskharon R, Oh SE (2016) Toxicity assessment using different bioassays and microbial biosensors. Environ Int 92–93:106–118. https://doi.org/10.1016/j.envint.2016.03.003
12. Comstock SE, Boyer TH, Graf KC, Townsend TG (2010) Effect of landfill characteristics on leachate organic matter properties and coagulation treatability. Chemosphere 81(7):976–983. https://doi.org/10.1016/j.chemosphere.2010.07.030
13. Tatsi A, Zouboulis A, Matis K, Samaras P (2003) Coagulation–flocculation pretreatment of sanitary landfill leachates. Chemosphere 53(7):737–744. https://doi.org/10.1016/s0045-6535(03)00513-7
14. Mojiri A, Ziyang L, Tajuddin RM, Farraji H, Alifar N (2016) Co-treatment of landfill leachate and municipal wastewater using the ZELIAC/zeolite constructed wetland system. J Environ Manag 166:124–130. https://doi.org/10.1016/j.jenvman.2015.10.020
15. Ranjan K, Chakraborty S, Verma M, Iqbal J, Kumar RN (2016) Co-treatment of old landfill leachate and municipal wastewater in sequencing batch reactor (SBR): effect of landfill leachate concentration. Water Q Res J 51(4):377–387. https://doi.org/10.2166/wqrjc.2016.020
16. Erabee IK, Ahsan A, Jose B, Aziz MMA, Ng AWM, Idrus S, Daud NNN (2018) Adsorptive treatment of landfill leachate using activated carbon modified with three different methods. KSCE J Civ Eng 22(4):1083–1095. https://doi.org/10.1007/s12205-017-1430-z
17. Chávez RP, Pizarro ECC, Galiano YL (2019) Landfill leachate treatment using activated carbon obtained from coffee waste. Eng Sanit e Ambient 24(4):833–842. https://doi.org/10.1590/s1413-41522019178655
18. Dabaghian Z, Peyravi M, Jahanshahi M, Rad AS (2018) Potential of advanced nano-structured membranes for landfill leachate treatment: a review. ChemBioEng Rev 5(2):119–138. https://doi.org/10.1002/cben.201600020
19. Warsinger DM, Chakraborty S, Tow EW, Plumlee MH, Bellona C, Loutatidou S, Karimi L, Mikelonis AM, Achilli A, Ghassemi A, Padhye LP, Snyder SA, Curcio S, Vecitis CD, Arafat HA, Lienhard JH (2018) A review of polymeric membranes and processes for potable water reuse. Prog Polym Sci 81:209–237. https://doi.org/10.1016/j.progpolymsci.2018.01.004
20. Siyal AA, Bristow KL, ŠImůnek J (2012) Minimizing nitrogen leaching from furrow irrigation through novel fertilizer placement and soil surface management strategies. Agricult Water Manag 115:242–251. https://doi.org/10.1016/j.agwat.2012.09.008
21. Achak M, Elayadi F, Boumya W (2019) Chemical coagulation flocculation processes for removal of phenolic compounds from olive mill wastewater: a comprehensive review. Am J Appl Sci 16:59–91. https://doi.org/10.3844/ajassp.2019.59.91
22. Wei H, Gao B, Ren J, Li A, Yang H (2018) Coagulation/flocculation in dewatering of sludge: a review. Water Res 143:608–631. https://doi.org/10.1016/j.watres.2018.07.029
23. Lippi M, Gaudie Ley MBR, Mendez GP, Felix Cardoso RA Jr (2018) State of art of landfill leachate treatment: literature review and critical evaluation. Ciência e Nat 40:78. https://doi.org/10.5902/2179460x35239
24. Särkkä H, Bhatnagar A, Sillanpää M (2015) Recent developments of electro-oxidation in water treatment—a review. J Electroanalytical Chem 754:46–56. https://doi.org/10.1016/j.jelechem.2015.06.016
25. Miao L, Yang G, Tao T, Peng Y (2019) Recent advances in nitrogen removal from landfill leachate using biological treatments—A review. J Environ Manag 235:178–185. https://doi.org/10.1016/j.jenvman.2019.01.057
26. Song U, Waldman B, Park JS, Lee K, Park SJ, Lee EJ (2018) Improving the remediation capacity of a landfill leachate channel by selecting suitable macrophytes. J Hydro-Environ Res 20:31–37. https://doi.org/10.1016/j.jher.2018.04.005
27. Fedorov K, Dinesh K, Sun X, Soltani RD, Wang Z, Sonawane S, Boczkaj G (2020) Synergistic effects of hybrid advanced oxidation processes (AOPs) based on hydrodynamic cavitation phenomenon—a review. Chem Eng J 432:134191. https://doi.org/10.1016/j.cej.2021.134191

28. Wu C, Chen W, Gu Z, Li Q (2021) A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment. Science Total Environ 762:143131. https://doi.org/10.1016/j.scitotenv.2020.143131
29. Kelly PT, He Z (2014) Understanding the application niche of microbial fuel cells in a cheese wastewater treatment process. Biores Technol 157:154–160. https://doi.org/10.1016/j.biortech.2014.01.085
30. Pant D, van Bogaert G, Diels L, Vanbroekhoven K (2010) A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Biores Technol 101(6):1533–1543. https://doi.org/10.1016/j.biortech.2009.10.017
31. Zairi M, Aydi A, Dhia HB (2013) Leachate generation and biogas energy recovery in the Jebel Chakir municipal solid waste landfill, Tunisia. J Mater Cycles Waste Manag 16(1):141–150. https://doi.org/10.1007/s10163-013-0164-3
32. Zou S, He Z (2018) Efficiently "pumping out" value-added resources from wastewater by bioelectrochemical systems: a review from energy perspectives. Water Res 131:62–73
33. Cai T, Huang M, Huang Y, Zheng W (2019) Enhanced performance of microbial fuel cells by electrospinning carbon nanofibers hybrid carbon nanotubes composite anode. Int J Hydrogen Energy 44(5):3088–3098. https://doi.org/10.1016/j.ijhydene.2018.11.205
34. Cai T, Huang Y, Huang M, Xi Y, Pang D, Zhang W (2019) Enhancing oxygen reduction reaction of supercapacitor microbial fuel cells with electrospun carbon nanofibers composite cathode. Chem Eng J 371:544–553. https://doi.org/10.1016/j.cej.2019.04.025
35. Li X, Klaus S, Bott C, He Z (2018) Status, challenges, and perspectives of mainstream nitritation-anammox for wastewater treatment. Water Environ Res 90(7):634–649. https://doi.org/10.2175/106143017x15131012153112
36. Yu F, Wang C, Ma J (2018) Capacitance-enhanced 3D grapheme anode for microbial fuel cell with long-time electricity generation stability. Electrochim Acta 259:1059–1067
37. Zhang F, Li J, He Z (2014) A new method for nutrients removal and recovery from wastewater using a bioelectrochemical system. Biores Technol 166:630–634. https://doi.org/10.1016/j.biortech.2014.05.105
38. Arends JBA, Verstraete W (2011) 100 years of microbial electricity production: three concepts for the future. Microb Biotechnol 5(3):333–346. https://doi.org/10.1111/j.1751-7915.2011.00302.x
39. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337(6095):686–690. https://doi.org/10.1126/science.1217412
40. Mook WT, Aroua MKT, Chakrabarti MH, Noor IM, Irfan MF, Low CTJ (2013) A review on the effect of bio-electrodes on denitrification and organic matter removal processes in bio-electrochemical systems. J Ind Eng Chem 19(1):1–13. https://doi.org/10.1016/j.jiec.2012.07.004
41. Schröder U (2011) Discover the possibilities: microbial bioelectrochemical systems and the revival of a 100-year-old discovery. J Solid State Electrochem 15(7–8):1481–1486
42. Schröder U, Harnisch F, Angenent LT (2015) Microbial electrochemistry and technology: terminology and classification. Energy Environ Sci 8(2):513–519
43. Logan BE (2008) Microbial fuel cells, 1st edn. Wiley-Interscience
44. Scott K, Yu EH (2015) Microbial electrochemical and fuel cells: fundamentals and applications (Woodhead Publishing Series in Energy), 1st edn. Woodhead Publishing
45. Sun J, Cai B, Zhang Y, Peng Y, Chang K, Ning X, Liu G, Yao K, Wang Y, Yang Z, Liu J (2016) Regulation of biocathode microbial fuel cell performance with respect to azo dye degradation and electricity generation via the selection of anodic inoculum. Int J Hydrog Energy 41(9):5141–5150. https://doi.org/10.1016/j.ijhydene.2016.01.114
46. ElMekawy A, Srikanth S, Bajracharya S, Hegab HM, Nigam PS, Singh A, Mohan SV, Pant D (2015) Food and agricultural wastes as substrates for bioelectrochemical system (BES): the synchronized recovery of sustainable energy and waste treatment. Food Res Int 73:213–225. https://doi.org/10.1016/j.foodres.2014.11.045

47. Feng C, Huang L, Yu H, Yi X, Wei C (2015) Simultaneous phenol removal, nitrification and denitrification using microbial fuel cell technology. Water Res 76:160–170. https://doi.org/10.1016/j.watres.2015.03.001
48. Hassan M, Wei H, Qiu H, Su Y, Jaafry SWH, Zhan L, Xie B (2018) Power generation and pollutants removal from landfill leachate in microbial fuel cell: variation and influence of anodic microbiomes. Bioresour Technol 247:434–442. https://doi.org/10.1016/j.biortech.2017.09.124
49. Hernández-Flores G, Poggi-Varaldo HM, Solorza-Feria O, Romero-Castañón T, Ríos-Leal E, Galíndez-Mayer J, Esparza-García F (2015). Batch operation of a microbial fuel cell equipped with alternative proton exchange membrane. Int J Hydrog Energy 40(48):17323–17331. https://doi.org/10.1016/j.ijhydene.2015.06.057
50. Champavert J, Innocent C (2015) Promising graphene modified electrode using layer-by-layer method for microbial biofilm connection. J Chem Chem Eng 9(5). https://doi.org/10.17265/1934-7375/2015.05.001
51. Rabaey K, Verstraete W (2005) Microbial fuel cells: novel biotechnology for energy generation. Trends Biotechnol 23(6):291–298. https://doi.org/10.1016/j.tibtech.2005.04.008
52. Li S, Chen G (2018a) Effects of evolving quality of landfill leachate on microbial fuel cell performance. Waste Manag Res 36(1):59–67
53. Li S, Chen G (2018b) Factors affecting the effectiveness of bioelectrochemical system applications: data synthesis and meta-analysis. Batteries 4(3):34
54. Ding W, Cheng S, Yu L, Huang H (2017) Effective swine wastewater treatment by combining microbial fuel cells with flocculation. Chemosphere 182:567–573
55. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25(5):464–482. https://doi.org/10.1016/j.biotechadv.2007.05.004
56. Sonawane JM, Adeloju SB, Ghosh PC (2017) Landfill leachate: a promising substrate for microbial fuel cells. Int J Hydrog Energy 42(37):23794–23798. https://doi.org/10.1016/j.ijhydene.2017.03.137
57. Vázquez-Larios AL, Poggi-Varaldo HM, Solorza-Feria O, Rinderknecht-Seijas N (2015) Effect of type of inoculum on microbial fuel cell performance that used RuxMoySez as cathodic catalyst. Int J Hydrog Energy 40(48):17402–17412. https://doi.org/10.1016/j.ijhydene.2015.09.143
58. Galvez A, Greenman J, Ieropoulos I (2009) Landfill leachate treatment with microbial fuel cells; scale-up through plurality. Bioresour Technol 100(21):5085–5091
59. Hernandez-Flores G, Solorza-Feria O, Poggi-Varaldo HM (2017a) Bioelectricity generation from wastewater and actual landfill leachates: a multivariate analysis using principal component analysis. Int J Hydrogen Energy 42(32):20772–20782
60. Zhang JN, Zhao QL, You SJ, Jiang JQ, Ren NQ (2008) Continuous electricity production from leachate in a novel upflow air-cathode membrane-free microbial fuel cell. Water Sci Technol 57(7):1017–1021. https://doi.org/10.2166/wst.2008.063
61. Hernandez-Flores G, Poggi-Varaldo HM, Romero-Castañón T, Solorza-Feria O, Rinderknecht-Seijas N (2017b) Harvesting energy from leachates in microbial fuel cells using an anion exchange membrane. Int J Hydrogen Energy 42(51):30374–30382
62. Ganesh K, Jambeck JR (2013) Treatment of landfill leachate using microbial fuel cells: alternative anodes and semi-continuous operation. Biores Technol 139:383–387. https://doi.org/10.1016/j.biortech.2013.04.013
63. Gálvez A, Greenman J, Ieropoulos I (2009) Landfill leachate treatment with microbial fuel cells; scale-up through plurality. Bioresour Technol 100(21):5085–5091. https://doi.org/10.1016/j.biortech.2009.05.061
64. Nguyen HTH, Min B (2020) Leachate treatment and electricity generation using an algae-cathode microbial fuel cell with continuous flow through the chambers in series. Sci Tot Environ 723:138054. https://doi.org/10.1016/j.scitotenv.2020.138054
65. Zaman B, Wardhana I (2018) Potential of electric power production from microbial fuel cell (MFC) in evapotranspiration reactor for leachate treatment using Alocasia Macrorrhiza plant

and Eleusine Indica grass. In: E3S web of conferences, vol 31, p 2010. https://doi.org/10.1051/e3sconf/20183102010
66. Zhen G, Kobayashi T, Lu X, Kumar G, Hu Y, Bakonyi P et al (2016c) Recovery of biohydrogen in a single chamber microbial electrohydrogenesis cell using liquid fraction of pressed municipal solid waste (LPW) as substrate. Int J Hydrogen Energy 41(40):17896–17906
67. Mahmoud M, Parameswaran P, Torres CI, Rittmann BE (2014) Fermentation pre-treatment of landfill leachate for enhanced electron recovery in a microbial electrolysis cell. Biores Technol 151:151–158. https://doi.org/10.1016/j.biortech.2013.10.053
68. Nguyen HT, Kakarla R, Min B (2017) Algae cathode microbial fuel cells for electricity generation and nutrient removal from landfill leachate wastewater. Int J Hydrog Energy 42(49):29433–29442. https://doi.org/10.1016/j.ijhydene.2017.10.011
69. Lee Y, Martin L, Grasel P, Tawfiq K, Chen G (2013) Power generation and nitrogen removal of landfill leachate using microbial fuel cell technology. Environ Technol 34(17–20):2727–2736
70. Khan N, Anwer AH, Ahmad A, Sabir S, Khan MZ (2020) Investigating microbial fuel cell aided bio-remediation of mixed phenolic contaminants under oxic and anoxic environments. Biochem Eng J 155:107485. https://doi.org/10.1016/j.bej.2019.107485
71. Zhang Q, Hu J, Lee DJ (2016) Microbial fuel cells as pollutant treatment units: research updates. Biores Technol 217:121–128. https://doi.org/10.1016/j.biortech.2016.02.006
72. Zhang G, Jiao Y, Lee DJ (2015b) A lab-scale anoxic/oxic-bioelectrochemical reactor for leachate treatments. Bioresour Technol 186:97–105
73. Zhang G, Jiao Y, Lee DJ (2015c) Transformation of dissolved organic matters in landfill leachate bioelectrochemical system. Bioresour Technol 191:350–354
74. You SHIJ, Zhao QL, Jiang JUNQ, Zhang JINN, Zhao SHIQ (2006) Sustainable approach for leachate treatment: electricity generation in microbial fuel cell. J Environ Sci Health Part A 41(12):2721–2734. https://doi.org/10.1080/10934520600966284
75. Huang L, Li X, Cai T, Huang M (2018) Electrochemical performance and community structure in three microbial fuel cells treating landfill leachate. Process Safety Environ Protect 113:378–387. https://doi.org/10.1016/j.psep.2017.11.008
76. Alabiad I, Md Ali U, Zakarya IA, Ibrahim N, Radzi R, Zulkurnai N, Azmi N (2017) Ammonia removal via microbial fuel cell (MFC) dynamic reactor. IOP Conf Ser: Mater Sci Eng 206:12079. https://doi.org/10.1088/1757-899X/206/1/012079
77. Li S, Chen G (2017) Effects of evolving quality of landfill leachate on microbial fuel cell performance. Waste Manag Res 36(1):59–67. https://doi.org/10.1177/0734242X17739969
78. Kumar SS, Malyan SK, Basu S, Bishnoi NR (2017) Syntrophic association and performance of Clostridium, Desulfovibrio, Aeromonas and Tetrathiobacter as anodic biocatalysts for bioelectricity generation in dual chamber microbial fuel cell. Environ Sci Pollut Res 24(19):16019–16030. https://doi.org/10.1007/s11356-017-9112-4
79. Cai PJ, Xiao X, He YR, Li WW, Zang GL, Sheng GP, Hon-Wah Lam M, Yu L, Yu HQ (2013) Reactive oxygen species (ROS) generated by cyanobacteria act as an electron acceptor in the biocathode of a bio-electrochemical system. Biosens Bioelectron 39(1):306–310. https://doi.org/10.1016/j.bios.2012.06.058
80. Liu T, Rao L, Yuan Y, Zhuang L (2015) Bioelectricity generation in a microbial fuel cell with a self-sustainable photocathode. Sci World J 2015:1–8. https://doi.org/10.1155/2015/864568
81. Saratale RG, Kuppam C, Mudhoo A, Saratale GD, Periyasamy S, Zhen G, Koók L, Bakonyi P, Nemestóthy N, Kumar G (2017) Bioelectrochemical systems using microalgae—A concise research update. Chemosphere 177:35–43. https://doi.org/10.1016/j.chemosphere.2017.02.132
82. Cui Y, Rashid N, Hu N, Rehman MSU, Han JI (2014) Electricity generation and microalgae cultivation in microbial fuel cell using microalgae-enriched anode and bio-cathode. Energy Conv Manag 79:674–680. https://doi.org/10.1016/j.enconman.2013.12.032
83. Lee DJ, Chang JS, Lai JY (2015) Microalgae—Microbial fuel cell: a mini review. Biores Technol 198:891–895. https://doi.org/10.1016/j.biortech.2015.09.061
84. Shukla M, Kumar S (2018) Algal growth in photosynthetic algal microbial fuel cell and its subsequent utilization for biofuels. Renew Sustain Energy Rev 82:402–414. https://doi.org/10.1016/j.rser.2017.09.067

85. Mohan SV, Srikanth S, Chiranjeevi P, Arora S, Chandra R (2014) Algal biocathode for in situ terminal electron acceptor (TEA) production: synergetic association of bacteria-microalgae metabolism for the functioning of biofuel cell. Bioresour Technol 166:566–574. https://doi.org/10.1016/j.biortech.2014.05.081
86. Kartal B, van Niftrik L, Sliekers O, Schmid MC, Schmidt I, van de Pas-Schoonen K, Cirpus I, van der Star W, van Loosdrecht M, Abma W, Kuenen JG, Mulder JW, Jetten MSM, den Camp HO, Strous M, van de Vossenberg J (2004) Application, eco-physiology and biodiversity of anaerobic ammonium-oxidizing bacteria. Rev Environ Sci Bio/Technol 3(3):255–264. https://doi.org/10.1007/s11157-004-7247-5
87. Li X, Sung S (2015) Development of the combined nitritation–anammox process in an upflow anaerobic sludge blanket (UASB) reactor with anammox granules. Chem Eng J 281:837–843. https://doi.org/10.1016/j.cej.2015.07.016
88. Li C, Ren H, Xu M, Cao J (2015) Study on anaerobic ammonium oxidation process coupled with denitrification microbial fuel cells (MFCs) and its microbial community analysis. Bioresour Technol 175:545–552
89. Li J, Li J, Gao R, Wang M, Yang L, Wang X et al (2018) A critical review of one-stage anammox processes for treating industrial wastewater: optimization strategies based on key functional microorganisms. Bioresour Technol 265:498–505
90. Ganigue R, Gabarro J, Lopez H, Ruscalleda M, Balaguer MD, Colprim J (2010) Combining partial nitritation and heterotrophic denitritation for the treatment of landfill leachate previous to an anammox reactor. Water Sci Technol 61(8):1949–1955
91. Yuan C, Lu C, Ma Y, Wang Y, Xie Y, Zhang K et al (2019) A novel method to treat old landfill leachate combining multi-stage biological contact oxidation (MBCO) and single-stage autotrophic nitrogen removal using anammox and partial nitrification (SNAP). Chem Eng J 359:1635–1643
92. de Vrieze J, Arends JB, Verbeeck K, Gildemyn S, Rabaey K (2018) Interfacing anaerobic digestion with (bio)electrochemical systems: potentials and challenges. Water Res 146:244–255. https://doi.org/10.1016/j.watres.2018.08.045
93. Tugtas AE, Cavdar P, Calli B (2013) Bio-electrochemical post-treatment of anaerobically treated landfill leachate. Biores Technol 128:266–272. https://doi.org/10.1016/j.biortech.2012.10.035
94. Dia O, Drogui P, Buelna G, Dubé R (2018) Hybrid process, electrocoagulation-biofiltration for landfill leachate treatment. Waste Manag 75:391–399. https://doi.org/10.1016/j.wasman.2018.02.016
95. Yong ZJ, Bashir MJ, Ng CA, Sethupathi S, Lim JW (2018) A sequential treatment of intermediate tropical landfill leachate using a sequencing batch reactor (SBR) and coagulation. J Environ Manag 205:244–252. https://doi.org/10.1016/j.jenvman.2017.09.068
96. Mandal P, Dubey BK, Gupta AK (2017) Review on landfill leachate treatment by electrochemical oxidation: drawbacks, challenges and future scope. Waste Manag 69:250–273
97. Kumar SS, Kumar V, Kumar R, Malyan SK, Bishnoi NR (2019) Ferrous sulfate as an in-situ anodic coagulant for enhanced bioelectricity generation and COD removal from landfill leachate. Energy 176:570–581. https://doi.org/10.1016/j.energy.2019.04.014
98. Hassan M, Pous N, Xie B, Colprim J, Balaguer MD, Puig S (2017) Influence of iron species on integrated microbial fuel cell and electro-Fenton process treating landfill leachate. Chem Eng J 328:57–65. https://doi.org/10.1016/j.cej.2017.07.025
99. Hassan M, Pous N, Xie B, Colprim J, Balaguer MD, Puig S (2017) Employing microbial electrochemical technology-driven electro-fenton oxidation for the removal of recalcitrant organics from sanitary landfill leachate. Biores Technol 243:949–956. https://doi.org/10.1016/j.biortech.2017.07.042
100. Li W, Zhou Q, Hua T (2010) Removal of organic matter from landfill leachate by advanced oxidation processes: a review. Int J Chem Eng 2010:1–10. https://doi.org/10.1155/2010/270532
101. Wang D, Hou H, Hu J, Xu J, Huang L, Hu S, Liang S, Xiao K, Liu B, Yang J (2019) A bio-electro-Fenton system with a facile anti-biofouling air cathode for efficient degradation

of landfill leachate. Chemosphere 215:173–181. https://doi.org/10.1016/j.chemosphere.2018.10.018
102. Zhang X, Miao X, Li J, Li Z (2019) Evaluation of electricity production from Fenton oxidation pretreated sludge using a two-chamber microbial fuel cell. Chem Eng J 361:599–608. https://doi.org/10.1016/j.cej.2018.12.117
103. Feng CH, Li FB, Mai HJ, Li XZ (2010) Bio-electro-fenton process driven by microbial fuel cell for wastewater treatment. Environ Sci Technol 44(5):1875–1880. https://doi.org/10.1021/es9032925
104. Yong XY, Gu DY, Wu YD, Yan ZY, Zhou J, Wu XY, Wei P, Jia HH, Zheng T, Yong YC (2017) Bio-electron-fenton (BEF) process driven by microbial fuel cells for triphenyltin chloride (TPTC) degradation. J Hazard Mater 324:178–183. https://doi.org/10.1016/j.jhazmat.2016.10.047
105. Wang W, Lu Y, Luo H, Liu G, Zhang R, Jin S (2018) A microbial electro-fenton cell for removing carbamazepine in wastewater with electricity output. Water Res 139:58–65. https://doi.org/10.1016/j.watres.2018.03.066
106. Puig S, Serra M, Coma M, Balaguer MD, Colprim J (2011) Simultaneous domestic wastewater treatment and renewable energy production using microbial fuel cells (MFCs). Water Sci Technol 64(4):904–909. https://doi.org/10.2166/wst.2011.401
107. Arango L, Cuervo FM, González-Sánchez A, Buitrón G (2015) Effect of microalgae inoculation on the start-up of microalgae-bacteria systems treating municipal, piggery and digestate wastewaters. Water Sci Technol 73(3):687–696. https://doi.org/10.2166/wst.2015.544
108. Uggetti E, Sialve B, Trably E, Steyer JP (2014) Integrating microalgae production with anaerobic digestion: a biorefinery approach. Biofuels Bioprod Biorefin 8(4):516–529. https://doi.org/10.1002/bbb.1469
109. Qin M, Molitor H, Brazil B, Novak JT, He Z (2016) Recovery of nitrogen and water from landfill leachate by a microbial electrolysis cell-forward osmosis system. Biores Technol 200:485–492. https://doi.org/10.1016/j.biortech.2015.10.066
110. Wang H, Ren ZJ (2013) A comprehensive review of microbial electrochemical systems as a platform technology. Biotechnol Adv 31(8):1796–1807. https://doi.org/10.1016/j.biotechadv.2013.10.001
111. Feng Q, Xu L, Liu C, Wang H, Jiang Z, Xie Z, Liu Y, Yang Z, Qin Y (2020) Treatment of shale gas fracturing wastewater using microbial fuel cells: mixture of aging landfill leachate and traditional aerobic sludge as catholyte. J Clean Prod 269:121776. https://doi.org/10.1016/j.jclepro.2020.121776
112. Zhou J, Li M, Zhou W, Hu J, Long Y, Tsang YF, Zhou S (2020) Efficacy of electrode position in microbial fuel cell for simultaneous Cr(VI) reduction and bioelectricity production. Sci Total Environ 748:141425. https://doi.org/10.1016/j.scitotenv.2020.141425
113. Li Y, Lu A, Ding H, Wang X, Wang C, Zeng C et al (2010) Microbial fuel cells using natural pyrrhotite as the cathodic heterogeneous Fenton catalyst towards the degradation of biorefractory organics in landfill leachate. Electrochem Commun 12(7):944–947

Application of Microbial Fuel Cells as Biosensors

Abu Hashem, Khanom Simarani, Ab Rahman Marlinda, M. A. Motalib Hossain, Mohammad Al Mamun, and Mohd Rafie Johan

Abstract The Microbial Fuel Cell (MFC) is a contemporary technology that employs electrogenic microorganisms as a catalyst to convert chemical energy contained in the bonds of organic matter found in waste materials directly into electricity, without polluting the environment. An MFC is a bioelectrochemical system with unique characteristics that may be utilised for a number of purposes, including power generation, waste treatment and biosensors. Besides powering a wide range of electrical equipment, its advancements in chemical, electrochemical and microbiological characteristics have extended its applications in chemical generation, acid and alkali production, bioremediation, water desalination and other fields. Except for powering tiny sensor devices, MFCs encounter significant challenges in real-world use as power producers. In recent years, there has been a lot of research done to broaden the use of MFCs as biosensors. Unlike electrical applications, MFC biosensors have a good chance of becoming practical tools in a variety of analytical applications. MFCs-based biosensors are gaining popularity in various fields due to their ease of application and long-term viability in quality monitoring of the environment. This

A. Hashem (✉) · A. R. Marlinda · M. A. M. Hossain · M. Al Mamun · M. R. Johan
Nanotechnology and Catalysis Research Centre, Institute for Advanced Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia
e-mail: hashemnib04@yahoo.com

A. R. Marlinda
e-mail: marlinda@um.edu.my

M. R. Johan
e-mail: mrafiej@um.edu.my

A. Hashem
Microbial Biotechnology Division, National Institute of Biotechnology, 1349 Ganakbari, Ashulia, Savar, Dhaka, Bangladesh

K. Simarani
Department of Microbiology, Institute of Biological Sciences, Faculty of Sciences, University of Malaya, 50603 Kuala Lumpur, Malaysia
e-mail: hanom_ss@um.edu.my

M. Al Mamun
Department of Chemistry, Jagannath University, Dhaka 1100, Bangladesh

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_17

chapter examines the most recent advancements in MFC-based biosensors in terms of their concepts, principles, design, operating mechanisms, power sources, power generation process, along with their scope and benefits. We also highlight biosensing applications in a variety of disciplines, with a focus on the detection of biochemical oxygen demand (BOD), toxicity, microbial activity, biocorrosion-causing microbial biofilms, volatile fatty acids, etc. A brief discussion of the problems and opportunities of MFC-based biosensors is also included.

Keywords Biosensor · BOD · Detection · MFC · Environmental monitoring · Toxicity

1 Introduction

The rise of the industrial revolution, urbanisation and a scarcity of crude oil have prompted scientists to search for other energy sources. The development of ecologically friendly, sustainable and renewable energy supplies is required as a result of the current energy crisis and global warming. Solar, wind, biomass and nuclear energy are all examples of non-conventional, carbon-neutral energy sources that are being researched and used to a large extent. Microbial fuel cells (MFCs) have arisen as the next viable and environmentally benign energy source [116]. Exoelectrogenic bacteria that function as substrate oxidation half-reaction catalysers in MFCs directly transform the chemical energy available in an organic bioconvertible substrate into electric energy [27]. It immediately transforms chemical energy contained in the bonds of organic materials in wastes into electricity without polluting the environment [113, 116, 133]. MFCs may decrease environmental pollutants such as waste, reduce atmospheric carbon dioxide, and offer a renewable source of electricity all at the same time [41].

Electrode-reducing organisms are those that transport electrons from the cathode to the anode. They can transmit electrons directly through their outer membrane proteins, a mediator molecule in the solution or nanowires/pili overlaying the bacterium's outer surface. Electrode-oxidising organisms use electrons from the cathode to convert CO_2 to acetate, for example [41].

In MFCs, microorganisms release electrons via substrate oxidation in the anode chamber, which are then transported to the cathode compartment via a conductive substance. The electrons interact with O_2 at the cathode, and the protons are diffused across a proton exchange membrane. MFCs require a constant flow of electrons in the anode and a constant flow of electrons in the cathode. The difference between the anode voltage and the substrate redox potential determines how much metabolic energy bacteria can acquire [19]. The generated biofilm in the anodic chamber serves as the bioreceptor in an MFC-based biosensor, while the anode serves as the transducer. The electron flow rate is affected by the anodic biofilm's reaction to the disturbance, which is translated into a quantifiable signal [43].

Due to the vast range of applications, such as disease detection, health care, drug delivery, food quality and water quality monitoring and environmental monitoring, biosensor design and development has taken centre stage for researchers in recent decades [112]. The MFC biosensors, which are based on the activity of microorganisms in MFCs, have received much interest as a consequence of the fast development of microbiology and have become an alternate tool for rapid, sensitive and selective recognition of numerous analytes [44, 174]. It has evolved into one of the most significant ecological monitoring techniques [47]. Because of its capacity to self-regenerate and self-replicate, the whole-cell biosensor has a lot of potential for making cost-effective and long-term environmental monitoring. It has the exclusive capacity to provide bioavailability information, which is impossible to get using any other analytical approach [47, 143, 174]. Fluorescent proteins, fluorescence molecules and enzyme activity are commonly used as indicators in conventional whole-cell biosensors. These marker molecules should be assessed utilising electrically driven apparatus such as microscopes, spectrometers and other instruments to get a quantitative signal [47, 174]. The biosensor's response will then be represented by the equipment's measured electrical output. Traditional biosensors require an external power supply and expensive equipment, which severely limits their use in distant and long-standing environmental monitoring when a sufficient power supply and necessary analytical instruments are frequently unavailable.

MFC technology is a unique way of utilising bacteria to generate bioelectricity from organic waste and renewable biomass [97], which may be used directly in biosensing. MFC-based biosensors have piqued interest currently owing to benefits such as high stability, sensitivity and distant place applicability with no electrical supply, regardless of their role in wastewater treatment or energy production [10]. Because of its simplicity and long-term viability, MFC-based biosensors have received much interest in recent decades, with applications ranging from water quality monitoring (e.g. poisonous substance) to air quality monitoring (e.g. CO_2) [43]. These MFC biosensors can detect characteristics and events in their environment and transform that information into signals. One of the most potential usages of MFC-allied technologies is the MFC-based biosensor, which has been investigated to quantity a range of parameters such as biochemical oxygen demand (BOD), dissolved oxygen (DO), chemical oxygen demand (COD), toxicants, microbial activity and volatile fatty acids (VFAs), among others [43].

In this chapter, we summarise the fundamentals, design, power sources, mechanism of electron transfer and operation of MFCs-based biosensors along with their application in various fields focusing on BOD, COD, VFAs, DO, toxicants, microbial activity, etc. Lastly, the further challenges and prospects of MFC-based biosensors in real time and onsite monitoring are also discussed.

2 Fundamentals, Configuration and Operation of Biosensors

2.1 Basic Principle of MFCs as Biosensors

A biosensor comprises three functional elements. A biorecognition element, a transducer and an electrical device with an amplifier, CPU and display are among the components [61]. The first part of the biosensor is the biological component, which is responsible for sensing the analyte and producing a signal. The biological component's response is then transmuted into a measurable signal by the second unit, the transducer, that is, the utmost important element in any sensing device. The detector, which magnifies and analyses the signals prior to presenting them on an electronic display device, is the biosensor's third component [122]. The different phases of a biosensor's signal processing, from sensing to transduction to display, as well as various types of bioreceptors and transducers, are depicted graphically in Fig. 1.

A biosensor is a system that joins a receptor and a transducer to transform a biochemical response into an electrical signal. MFCs are devices that employ metabolic activities of microorganisms to directly transform chemical energy in organic materials into electricity. An MFC consists of two electrodes, an anode and a cathode, that are connected by an electrolyte. An ion/proton exchange membrane (PEM) separates the electrodes, which are linked via an exterior circuit that contains an external load (Fig. 2). Anodophiles (electroactive bacteria) live as a biofilm on the device's anode, which functions as a bioreceptor. The anodophiles generate electrons,

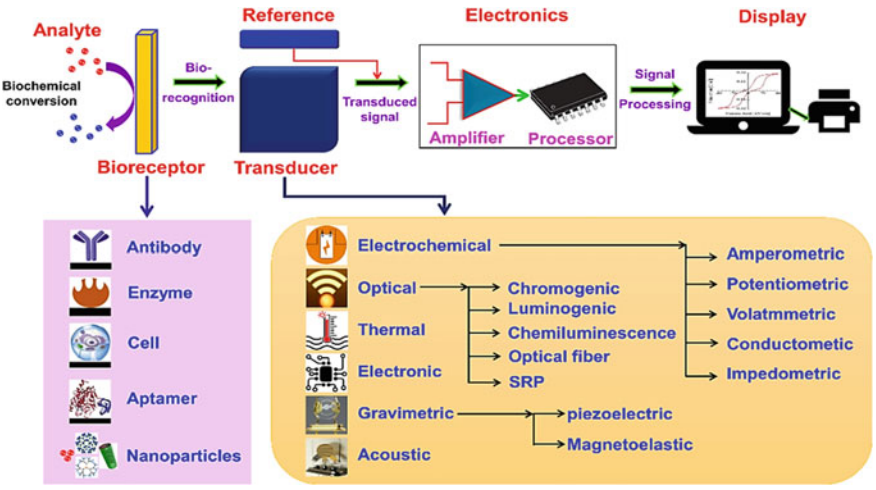

Fig. 1 A schematic illustration of a typical biosensor, which includes a bioreceptor, transducer, electrical system (amplifier followed by processor) and display (PC or printer), as well as numerous types of bioreceptors and transducers. Reprinted from Ref. [112] with permission under Creative Commons Attribution (CC BY) license

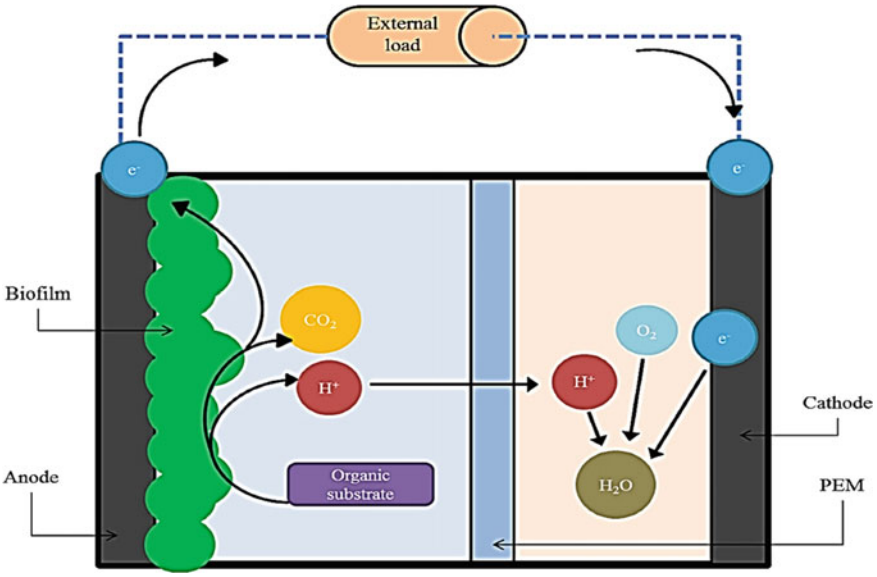

Fig. 2 A two-compartment MFC's operating principles. The anode's electroactive biofilm degrades an organic substrate, producing electrons, protons and CO_2. The electrons are reduced by the cathode after passing through an external circuit. Reprinted from Ref. [40] under the Creative Commons Attribution License

protons and CO_2 by oxidising the biodegradable organic molecules in the feed solution. Electrons are extracellularly transported to the anode and travel via the exterior circuit in the direction of the cathode in the absence of oxygen, generating electricity. Water is formed when protons move via the PEM towards the cathode and combine with electrons and an electron acceptor (typically oxygen). The current produced by an MFC is directly proportional to the metabolic action of the electroactive biofilm on the anode shell. Any disruptions in their metabolic routes result in a change in the amount of power produced. This current variation may be linked to the precise disturbance applied if operational factors like temperature, pH and conductivity of the feeding fluid are maintained steady. The usage of MFCs as electrochemical microbial biosensors is based on this principle [40].

MFCs are electrochemical systems that employ the redox metabolic processes of microbes to produce electricity. If the microorganisms in the anodic compartment are biologically active and there is a useable carbon supply, they produce a voltage discrepancy between the anode and the cathode, ensuring an electron flow driving force. This is the property that makes MFCs suitable for biosensor functions [32, 70, 82]. The anode compartment microorganisms function as biocatalysts, while the electrodes and PEM serve as transducers. Two essential ideas underpin the practical uses of MFC-based biosensors. The objective in the first circumstance is to find contaminated microbes. As a result, a sample's sterility may be continuously monitored and reported. A positive signal (electron production) is generated when a

contaminating microbe appears, but no signal is observed in a sterile sample. In the second example, biosensing may be used to monitor the presence or appearance of a target chemical when a specific bacteria strain is employed as an essential element of a system that is sensitive to that chemical [40] by measuring the strength of the electrical signal generated during microorganism metabolism.

2.2 *Design and Configuration*

Electrodes, their connections, cells and a salt bridge are the fundamental components of MFCs. An ion exchange membrane replaces the salt bridge in a PEM in MFC. The system's efficiency and mobility have been improved by improving its handling, cost and power generation. A two-chamber MFC typically comprises an anode and a cathode compartment divided by a PEM, as illustrated in Fig. 3, but exposure of the cathode element directly to the open air removes the requirement for the cathodic portion in a single chamber. A two-chamber MFC, on the other hand, works in the water-cathode mode, while a single-chamber MFC works in the air-cathode mode. The main benefit of the two-chamber MFC over the one chamber is that the cathode's functioning may be increased by regulating purging pure O_2, improving the flow rate, changing pH and supplying electron mediators to the cathode, resulting in total MFC performance improvement. Almost all current configurations are based on three primary configurations, which will be offered greater attention since they are critical to the MFC-based biosensor's history [55]. Customising the reactor configurations

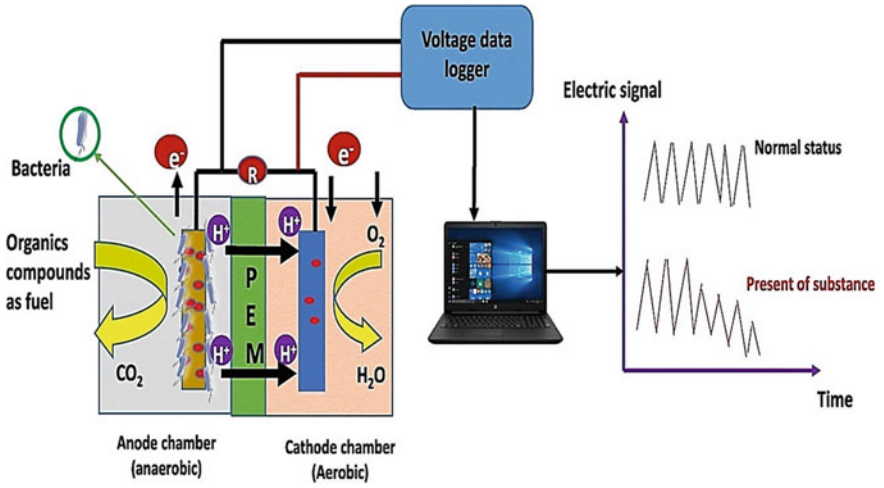

Fig. 3 Design architecture and basic components of the double-chamber MFCs-based biosensor. Reprinted from Ref. [46] with permission. Copyright (2020) Elsevier

can enhance the performance of MFCs. The success of microbial fuel cell (MFC)-based biosensors is determined on the assemble and configuration of the fuel cell.

MFCs are systems that transform biochemical energy directly into electricity employing microorganisms as catalysts. The single-chamber MFCs [94] which have developed from the original double-chamber layout in an effort to abolish a membrane are primarily made up of anodic chambers [26]. The single-chamber devices may also yield the best results. A basic MFC model can be single or double chambered depending on how the anode and cathode chambers are assembled. Aside from these two fundamental concepts, numerous design and structural changes have been done to improve the MFC prototype [119]. They are categorised into two forms based on their configuration: single-chamber MFCs and double-chamber MFCs.

Double-Chambered MFCs: In principle, a PEM separates the anodic and cathodic chambers of a double-chambered MFC, allowing proton movement from the anode towards the cathode while inhibiting O_2 passage into the anode. As a result, this arrangement is widely utilised to treat waste and create electricity at the same time, which is useful in biosensing. Both the anode and the cathode are distinct compartments that are linked by a PEM which serves primarily as a proton transmission channel to complete the circuit between the two compartments [13, 176] (Fig. 3). This completes the reaction and inhibits the diffusion of O_2 or any other oxidants from the cathode chamber. Double-chambered MFCs provide energy power output in a batch manner with a chemically specified medium such as an organic substrate solution [55] and can be used in biosensing.

Single-Chambered MFCs: The idea behind the construction of a single-chambered MFC, in which the anodic compartment is connected to a porous air exposed cathode, and they are separated from one another a PEM or by a gas diffusion layer, allowing passive O_2 transport to the cathode. To complete the circuit, electrons are delivered to the porous cathode across an electrically conducting wire. Because the use of O_2 as a last electron acceptor eliminates the requirement to aerate the cathode, single-chamber MFCs with an air-cathode assemblage have been developed. Researchers are interested in this sort of MFC arrangement (Fig. 4) because of numerous advantages, including lower internal resistance, simplicity of operation, increased O_2 reduction amount on the cathode, improved proton circulation and decreased electrode spacing. This arrangement is more flexible since it requires less frequent regular change of oxidative medium and aeration [55].

Electroactive microorganisms are introduced into the anodic chamber, where they oxidise organic molecules to make electrons and protons. The anode captures electrons, which are subsequently sent through an exterior circuit to the cathode. To maintain charge balance, protons and other positive ion like K^+, Na^+ transfer to the cathode via the PEM [73]. Finally, oxygen serves as an electron acceptor, allowing electrons and protons to merge to produce water [15, 183].

Although lot of variations are available, there are mainly three groups of microbial biosensors categorised based on signal transducers: electrochemical, optical and MFCs [166]. The alter in electric potential, current and conductivity induced by microbial-analyte interaction is exploited by electrochemical transducers. Biosensors

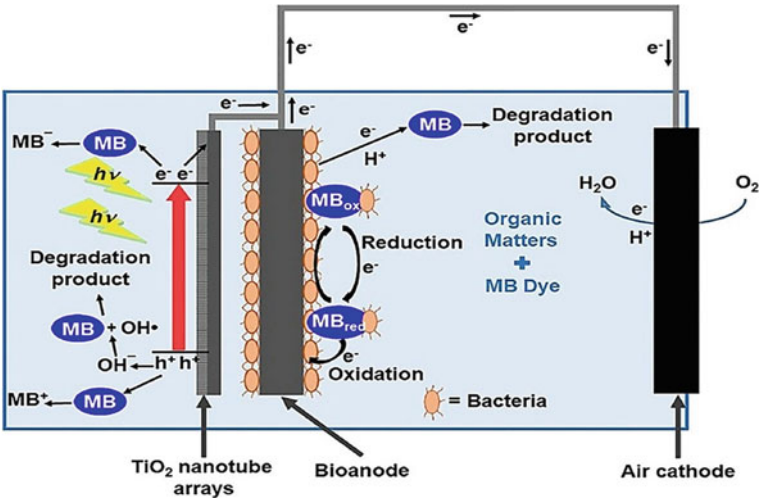

Fig. 4 Design the architecture and basic components of an MFCs-based single-chambered biosensor. Reprinted from Ref. [84] with permission. Copyright (2018) Elsevier

can be classified as potentiometric, amperometric or conductometric. The potentiometric transducer was developed by Mulchandani [111]. Ion selective electrodes are used in these transducers to convert the biochemical signal into an electrical signal. These are less sensitive, make greater relative errors and have a poor linear connection between the exported signal and the detected analyte concentration [166]. On the other hand, Amperometric microbial biosensors function at a set voltage in relation to a reference electrode, and the equivalent current is produced as a result of the oxidation or reduction of electroactive compounds on the electrode's surface [166]. This arrangement has been depicted by Yong et al. [173], Anu Prathap et al. [12] and Wang et al. [158], conductometric biosensors, as the name implies, measure changes in medium conductivity induced by the target analyte. Despite the fact that conductance quantification is highly sensitive, solution conductance detection is deemed nonspecific [166].

Sensor devices that employ optical principles such as bioluminescence, colorimetry and fluorescence to convert a biochemical interface into an appropriate output signal are known as optical biosensors [166]. The expression of bioluminescence and fluorescence in the target organism is possible thanks to genetic engineering. In biosensing, scientists explore the use of luciferase [29, 114, 142] and green fluorescent protein (GFP) applications [75, 159].

2.3 Operation/Working Mechanism

In 1910, Potter reported, 'the disintegration of organic compounds by microorganisms is accompanied by the liberation of electrical energy' [126]. Microbes perform metabolic processes (catabolism and anabolism) either in the accessibility of O_2 (aerobic) or in the inaccessibility of O_2 (anaerobic). Microbes use the accessible substrate (fermentation) by producing reducing equivalents [electrons (e^-)/protons (H^+] in the form of redox carriers, regardless of their metabolism. During respiration, these redox carriers assist in the generation of energy.

The chemical energy of decomposable organic compounds can be directly transformed into electrical energy in MFCs thanks to the metabolism of exoelectrogenic bacteria. The power produced can be quantified and/or used to build MFC-based biosensors for detecting decomposable organic compounds and/or hazardous compounds in water or wastewater [150]. The MFC works by oxidising organic materials using microorganisms as a biocatalyst [106]. In principle, bioelectrochemical systems may be used in self-contained effluent treatment amenities to convert wastewater, including organic materials, into electricity. Actually, bioelectrochemical systems can reduce the energy consumption of activated sludge treatment processes [50, 51] while simultaneously detecting them using MFC-based biosensors. The scientific idea is very appealing, and many research studies have been carried out in this area.

Unlike traditional sensors, bacteria in an MFC-based biosensor can sense the analyte and then respond to its output electric current, where the detection and electrical signal conversion steps are combined and can be accomplished in single phase without the use of a signal transducer or an outside energy source. The MFC-based biosensor's most intriguing feature is that it does not require a transducer to transform the output to an electric signal since the assessed signal is available as an electrical current. These distinct properties help to create disposable and portable biosensors that precisely suit the needs of long-term and distant sensing [148].

Microorganisms oxidise the substrate in the anode compartment of a conventional MFC, generating electrons that are then carried by the anode electrode across the exterior cable. The protons flow across the PEM while the electrons flow to the cathode. In the cathode, protons and electrons interact with O_2 to produce water [113]. Considering acetate as an organic substrate, the subsequent reaction occurs in MFC.

Anode half-cell reaction (in the presence of microbes):

$$CH_3COO^- + 4H_2O \rightarrow 2CO_2 + 9H^+ + 8e^- \quad (1)$$

After that, the generated electrons reduce electron acceptors such as O_2 at the cathode.

Cathode half-cell reaction:

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (2)$$

There are several essential considerations for using an MFC as a biosensor that may differ from those for using it to generate energy. When the goal is to produce electricity, the attention is on improving fuel efficacy and current production, but when the goal is to employ the MFC as a biosensor, the aim will be on more sensitive recognition of the target chemicals [95]. The variation in electric signal per unit of change in analyte content concentration is defined as sensitivity, which is generally controlled by the anode's surface area (Eq. 3) [45].

$$\text{Sensitivity} = \frac{\Delta I}{\Delta c \times A} \tag{3}$$

Here, the difference in the current output is ΔI (μA), while the unit difference in the analyte content is Δc (mmol/l) and the surface area of the electrode is A (cm^2). As a result, better sensitivities are linked to differences in current per unit change in target concentration. The biosensor should also generate a consistent and continuous current output, referred to as the baseline [147]. As a result, it is critical to keep a monitor on the anode's overpotential and the feed pH in the MFC. Anode voltages between -0.4 and -0.35 V versus the Ag/AgCl reference electrode give the best steady output current density, according to prior research. In the long-term procedure, the MFC biosensor stability must be confirmed. The outputs of MFC biosensors should be reproducible regardless of operating factors including temperature, pH and conductivity of liquid samples [2]. Furthermore, in order to attain 95% of the steady-state current, the response time must be very fast. Following the fermentation/toxic response, the needed recovery period from the employed disturbance must be minimal, and the starting baseline current need to be entirely restored.

To comprehend the outputs of an MFC biosensor, the use of artificial neural networks (ANNs) was recommended. ANNs are a type of mathematical prototype utilised to assess complex nonlinear connections between input and output records. In a batch mode MFC, ANN was able to properly identify butyrate, acetate, glucose and corn starch [54]. This model provides an effective method for determining target analytes from MFC signal responses. The advantages of MFCs over other sorts of biosensors are due to their mechanical and electrical simplicity of operation and construction. Because the pollutant, which runs in the feeding stream, is immediately recognised by a defined current variation through the system, no extra transducers are necessary to transform the biochemical/organic reaction into a signal. MFC biosensors have been in continuous operation onsite, providing real-time monitoring. Furthermore, the MFCs' electrical power output makes them excellent for use as sustaining devices. They may be suitable for use in locations where there are no available energy sources [103].

3 Microbial Fuel Cells as Biosensors

The biosensors we have observed so far necessitate the use of a transducer that can convert bacterial analyte contact into a measurable signal. This necessitates expensive electrical equipment and external power supply, limiting the use of these biosensors in distant regions where external power is scarce. As a result, MFC-based biosensors have piqued the scientific community's interest as a viable alternative to conventional biosensors. MFCs were first conceived as a method of obtaining energy from the metabolic processes of anaerobic bacteria that oxidise organic molecules. However, because the MFCs' power output is so low, significant research has been done in recent years to identify alternate applications for the MFCs. Biosensing in environmental monitoring is one such potential application that has been thoroughly investigated. MFC-based biosensors might be utilised as self-powered portable biosensors with a lot of applications in long-standing and remote environmental monitoring [148].

The chemical energy of biodegradable compounds may be directly transformed into electricity in MFCs thanks to the metabolism of exoelectrogenic microbes. The produced electricity may be employed directly to build MFC-based biosensors for the identification and monitoring of biodegradable organic components available in the target samples [150]. The alternative perspective is that any toxicant in the feedstock solution would impact microbial metabolic activity, and thus substrate intake rate, which is directly linked to an MFC's current output. As a result, any variation in the availability and content of toxicants in flowing water can be easily identified by observing perturbations in the electric current produced by MFCs [141, 146], saving time and money over traditional methods [63]. MFCs that produce an electrical signal in reaction to any input analyte can be utilised as a biosensing application in this case.

The biologically energetic anaerobic bacterial species in the anodic compartment functions as a biocatalyst in MFCs, acting as the biosensor's biological detection element. In the presence of a metabolizable organic nutrient source, these anaerobic microbes produce a detectable voltage difference between the electrodes, resulting in an electron flow [108, 109]. There is a difference in current production based on the interaction with the analyte. MFCs that will be utilised as biosensors are based on this fluctuation in output current. The current generated in MFCs can function as a transducer element [154], which is measurable and depends on the electron transmission kinetics of the microbes, in addition to the analyte concentration [105]. This property of MFC-based biosensors, where the assessment and signal detection stages are combined, reduces the need for a transducer for signal conversion [148], thus enhancing the benefits of using MFC as a biosensorics. Aside from the fact that an MFC biosensor does not require a separate sensing element and transducer, these systems have the extra benefit of allowing for online monitoring in both the laboratory and field settings because they can be used in flow-through and assay formats [136]. Furthermore, their improved stability and sensitivity, as well as their capacity to detect a wide range of chemicals, make them excellent biosensors [169].

4 Selection of Microorganisms for MFCs-Based Biosensors

Most microbes are incapable to deliver enough electrons outside of cells to generate efficient current because their exterior layers consist of nonconducting lipid membranes, lipopolysaccharides and peptidoglycans that impede electron transmission to the anode [101]. A critical stage in the development of a microorganism-based biosensor is the assortment of an appropriate microbe for detecting contaminants and their effects in the environment, as well as its inclusion into a suitable transducer. The most often utilised microorganisms for biosensors are bacteria and yeast [166]. To provide cost-effective detection, the selected microorganism ought to be vigorous and capable of precise pollutant detection at low concentrations. Whole-cell biosensors [12, 29, 89] and MFCs [45, 89, 140] biosensors have recently received a lot of interest.

The recent discovery of a MFC that is capable of generating electricity from organic materials trapped in sediments has shown that generating reasonable amounts of electricity for biosensing in distant locations is possible. Microorganisms that totally oxidise organic substances to CO_2 with direct electron transmit to electrodes have been discovered. This means that biosensing might benefit from self-sustaining MFCs that can efficiently transform a huge variety of waste organic substances or recyclable biomass to electricity [98].

Some bacterial species such as *Shewanella spp.* [155] and *Clostridium butyricumcan* [121] have been demonstrated to be capable of self-mediating extracellular electron transfer utilising their own metabolites. In the meantime, direct electron transfer involving electroactive redox enzymes (cytochromes) has been found in several bacterial species, including *Shewanella oneidensis* [96], *Shewanella putrefaciens* [7], *Rhodoferax ferrireducens* [33], *Geobacter sulfurreducens* [21] and the oxygenic phototrophic cyanobacterium *Synechocystis sp.* PCC 6803 [58]. Exoelectrogens are bacteria that have developed electrically conducting molecular pili to enable direct electron transmission. *S. oneidensis* and *G. sulfurreducens* are two examples. *S. oneidensis* may also perform mediated electron transfer utilising a self-produced mediator, in addition to direct electron transfer. Exoelectrogens in MFCs are considered to actively utilise electrodes to preserve electrochemical energy needed for their development, ensuring elevated levels of fuel oxidation and electron transfer for electrical energy production [101].

In MFCs, a wide variety of microorganisms have been used as electron donors and acceptors. They include *Phormidium sp.*, *Chlorella vulgaris*, *Saccharomyces cerevisiae*, *Leptothrix discophora*, *Scenedesmus armatus*, *Rhodispirullum rubrum*, *Thiobacillus ferrooxidance*, *Desulfovibrio desulfuricans*, *Pseudomonas fluroscens*, *Geobacter metallireducens* and some anaerobic bacteria [10, 71]. Genetic engineering has also grown in importance. We can modify microorganisms to enhance analyte detection systems or express them in different ones [111]. DNA segments coding for detecting mechanisms may be isolated and introduced into prototype organisms such as *S. cerevisiae and Escherichia coli,* which have optimal growth conditions. To get the highest expected signal detection, the organism and detecting

configuration should be correctly integrated. Some of the species listed above have been genetically modified to generate considerably more current and long-term biomass production than their wild-type strains.

5 Power Sources of MFCs-Based Biosensors

Electrochemical batteries (e.g. lithium batteries) power the majority of commercial sensor and biosensor devices, which have a reduced and comparatively short life cycle and must be recharged or replaced on a regular basis [6]. To find out effective and self-renewable power supplies to generate adequate power for distant devices when battery substitution is neither possible nor accessible is a hot topic these days [48]. In this perspective, self-renewable MFCs seem to be a viable long-term energy source for remote monitoring biosensors and sensors. In distant sensors, supplanting traditional batteries with MFC power sources reduces operational costs and reduces environmental concerns significantly [63].

The MFC is a device in which microbes use organic substances as a nutrition supply, produce electrons/energy from the assimilation of organic compounds by microorganisms' metabolic activity and discharge those electrons to an electrode, which generates electricity [17, 62, 132]. An MFC is an electrochemical bioreactor that uses the unique characteristics of the colony of bacteria located within the MFC chamber to produce electrical energy. An MFC is made up of a pair of conductive electrodes with a bacterial habitat between them. The electrogenic bacteria employed determine the cell's specific voltage potential and maximum output power [28, 94]. The bacteria that inhabit the MFC release electrons as a result of their metabolism of organic substances available in the environment, and the amount of power provided is dependent on the colony's health and organic nutrient sources. It is essential to consider the MFC's influencing elements in order to get desired results. Microorganisms and their metabolism; substrates and their concentration; electrode element and electrode shape, membrane type;; mechanism of electron transfer in an anodic compartment; functioning parameters such as pH, temperature and salt concentration; cathodic compartment's electron acceptor and geometric layout of the MFC are the most vital parameters among the numerous factors affecting MFC performance in biosensing [5]. For the power supply of low-power embedded systems, MFC is a viable option to other fuel cells [22, 99] or accumulator technologies [125].

The hydrolysis of complex substrate such as proteins, carbohydrates and lipids in the anaerobic digestion chamber begins with the conversion of these molecules to hydrolysates which consists of amino acids, sugar and long-chain fatty acids. Hydrolytic microorganisms are the ones liable for this process. Hydrolysate conversion to simple organic acids, CO_2 and H_2 is the next step in anaerobic digestion, which is carried out by acidogens or fermentative bacteria. In the third phase of anaerobic digestion, acetogenic bacteria convert simple organic acids to acetate, carbon dioxide and hydrogen. The last phase in the anaerobic digestion method is the conversion of acetate to H_2O, CO_2 and electrons, which is carried out by electrogens, but

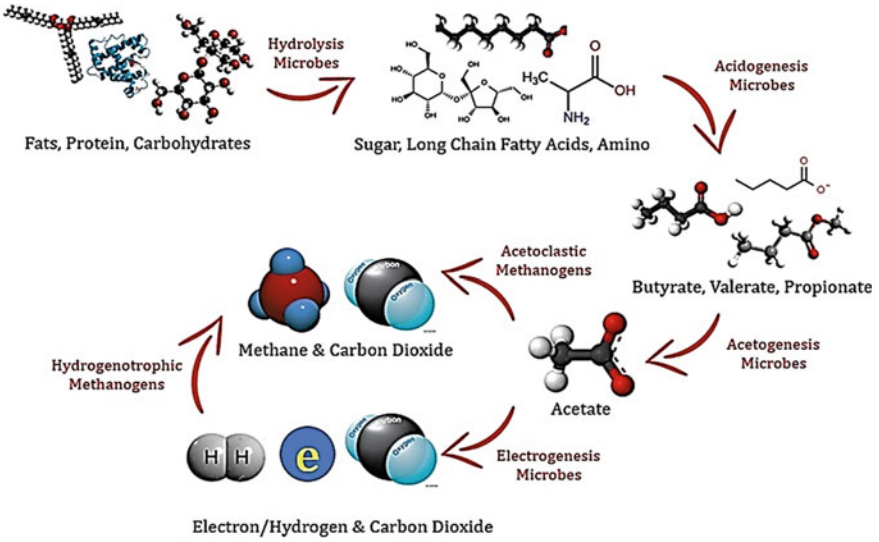

Fig. 5 The sequential biodegradation processes of a complex substrate by different microorganisms are for power generation in MFC-based biosensors. Reprinted from Ref. [14] with permission. Copyright (2021) Elsevier

acetoclastic methanogens can also convert acetate to methane and carbon dioxide. Furthermore, a kind of methanogen known as hydrogenotrophic methanogens may use electrogens to convert protons and carbon dioxide into methane [14, 18]. Figure 5. depicts the successive power-generating procedures. The electrons produced by this process are used in both the power production and biosensing processes.

For the bacteria to operate and release the charges/electrons that the cathode needs to complete the electricity generation, the anode must be placed in an oxygen-poor layer. The cathode, on the other hand, is positioned on top of the media or aeration chamber because it must exchange oxygen with the environment while combining positive charges and receiving electrons from an external circuit. This process produces water as a by-product. As far as bacteria absorb nutrients from the medium, this process works [23].

6 Mechanism of Electron Transfer in MFCs

Electrons must be transferred from interior microbial cell membrane to the outer surface for MFC to operate, as electrodes cannot penetrate cell membranes because they are solid things. This can be accomplished by (a) utilising electrons that leave the cell membrane via membrane-attached redox enzymes or (b) transferring reduced substances physically. The process of electron transport to the electrode, however, leads it towards redox-active units capable of creating electric connections between

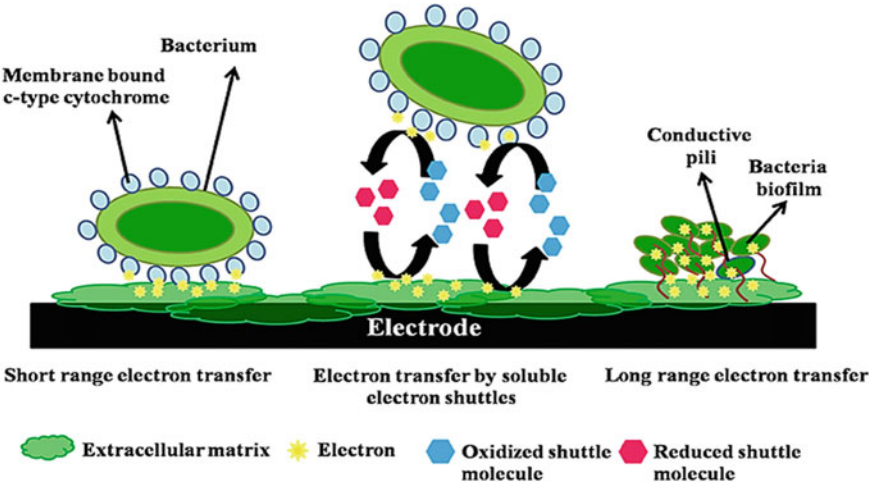

Fig. 6 Different mechanisms of electron transfer include short-range electron transfer via cytochrome b of the membrane (direct), electron shuttle mediated through intermediate molecules (indirect) and long-range electron transfers via the pili (direct) of a bacterium. Reprinted from Ref. [10] under Creative Commons Attribution License (CC BY)

the bacterial cell and the electrode [113]. Microorganisms can transport electrons to the electrodes via two major processes (Fig. 6).

6.1 Direct Electron Transfer

In the first kind of MFC, the bacterium directly transmits electrons from its membrane to the electrode, bypassing any intermediary fermentation product [88]. This is known as a direct transfer. Because these microorganisms are the catalysts in electron transfer, these MFCs need the use of a highly active microbial consortia, which can be mixed cultures. The transfer is facilitated by cytochrome proteins adsorbed on the bacterial cell wall. This kind of bacterium includes *Rhodoferax ferrireducens* [92] and *Geobacter sulfurreducens* [21].

The direct electron transfer method is based on the capability of several microbes, sometimes recognised as exoelectrogens, to carry electrons generated by organic matter oxidation directly to the anode. Bacterial membrane-bound-redox-active proteins (for example, c-type cytochromes and multi-heme proteins) and pili are both involved in this process [118]. The direct transfer of electrons produced during consumption from electroactive bacteria to the anode is the most significant process (Fig. 1). It was initially hypothesised that microorganisms might transport electrons to an electrode surface when cultures of *Shewanella putrefaciens* generated electrical energy while metabolising lactate [117]. *Shewanella putrefaciens* MR-1, a metal-reducing bacterium, was shown to pose cytochromes in its external surface.

These transport proteins (cytochromes) were able to produce anodic current in the absence of terminal electron acceptors in anaerobic settings. In *Shewanella*, it was also revealed that external membrane cytochromes play a role in electron shuttle reduction [157].

A variety of exoelectrogens have been described to use direct electron transfer pathways to transport electrons to the anode, although *Geobacter sulfurreducens* has been the most thoroughly investigated in this respect, owing to its genome being sequenced. Around 110 genes in the *G. sulfurreducens* genome are thought to encode for type-c cytochromes, which are supposed to perform a key function in extracellular electron transport mechanism [4]. A research found that a mediatorless MFC injected with *Desulfovibrio desulfuricans* and supplied with electrochemically cured graphite felt electrodes had the maximum current density of 233 mA/m^2. *D. desulfuricans* cytochrome-c was implicated in the effective transport of electrons to the electrode surface [68].

In single-layer biofilms, most of the cells are in tight proximity to electrodes and are therefore engaged in current generation directly. Because just a few cells may directly reach electrode surfaces in multiple layer biofilms, long-array electron transport techniques such as nanowire/pili are utilised. The thick pili network has metal-like conduction, which is responsible for conductive biofilms' high current production. Various bacteria, including *G. sulfurreducens*, generate conductive pili. The pili such as type-IV are nanowires engaged in the transfer of electrons between chambers in the biofilm and to the electrode's surface. Charge transmission from cell to cell through pili was recently demonstrated by electrostatic force microscopy to be comparable to that of carbon nanotubes [4].

In the case of heterogeneous cultures, exoelectrogens employ direct interspecies electron transfer for intermediate electron transmission. Direct interspecies electron transmission is facilitated by pilus and pilus-linked c-type cytochrome OmcS. Earlier transcriptomic and genetic investigations showed that *G. sulfurreducens* and *G. metallireducens* developed conductive aggregates when metabolising ethanol, and that the aggregates exchanged electrons during syntrophic interaction [34]. Tetrathiobacter, Clostridium, Aeromonas and Desulfovibrio anolyte communities were investigated for bioelectricity production. Proteobacteria and Firmicutes have a syntrophic relationship, according to community analysis. Fermentation and ferredoxin-facilitated electron transport to the electrode were both aided by Clostridium. Sulphate-reducing–sulphur-oxidising bacteria such as Aeromonas, Desulfovibrio and Tetrathiobacter transport electrons directly to the electrode [81].

6.2 Indirect Electron Transfer

Soluble molecules are used to mediate electron transport in indirect electron transfer. Artificial exogenous redox mediators and soluble electron shuttles produced by microbes are the two most common types of mediated electron transfer [25].

6.2.1 Using Artificial Exogenous Redox Mediators

A fermentative microbe generates alcohols, carbon dioxide, hydrogen or ammonia as by-products in an indirect MFC or mediator-based MFC. Electrons produced during substrate catabolism are utilised in anaerobic circumstances to reduce transitional products like protons or acid to make hydrogen or alcohol, correspondingly. As a result, the fermentative bacteria are unable to give electrons to the anode directly. An external mediator that can shuttle within the cell membrane and the anode is necessary to use this bacterium on the anode. Some typical exogenous electron mediators shuttling within the anode and the cell membrane of fermentative bacteria are thionine, benzylviologen, 2-hydroxy-1,4-naphthoquinone and 2,6-dichlorophenolindophenol [87] (Fig. 6).

Because of the numerous drawbacks involved with this strategy, it has been widely abandoned. Cohen suggested the use of inorganic or organic compounds such as benzoquinone or potassium ferricyanide to assist electron transport from cells to electrodes to solve the low current production problem in 1930 [42]. Benetto and his co-workers revived this technique in the 1980s, and it gained a lot of popularity. Because of their potential as mediators, a wide variety of molecules based on phenoxazine, quinones, phenazines and phenothiazine were chosen [113, 120].

Artificial mediators have a number of drawbacks, including low current densities (10–100 $\mu A/cm^2$) and the requirement for frequent supplements, which is both ecologically and technologically impractical. As a result of these drawbacks, this technique has mostly been abandoned. Artificial mediators are no longer required for mediated electron transfer using natural electron shuttles and direct electron transfer processes, according to most experts [25].

Soluble electron shuttles secreted by microorganisms

Bacteria without pili can generate electricity by secreting secondary metabolites such as pyocyanins, flavins and quinones, which function as endogenous soluble electron shuttles. These electron shuttles communicate with cytochromes to transport electrons to the electrode. *G. sulfurreducens* secretes riboflavin, which forms a connection with OM c-Cysts and therefore performs an essential part in the extracellular electron transfer mechanism [100]. *Pseoudomonas aeruginosa* strain KRPI was previously reported to generate phenazine-1-carboxamide and pyocyanin to transport electrons through the cell membrane. A glycolipid surfactant named Sophorolipid was recently introduced to the system, which improved the penetrability of the cell membrane and boosted pyocyanin synthesis. As a result, compared to the control, power output rose fourfold [138].

Microorganisms such as *Lactobacillus*, *Enterococcus* and *Pseudomonas aeruginosa* have been found to produce electron shuttles (i.e. phenazines by *Pseudomonas aeruginosa*) that aid in electron transport to the anode. *Shewanella oneidensis* has been found to use an electron shuttle-like mechanism to reduce extracellular Fe^{3+} [130]. The production of natural mediators such as riboflavin and pyocyanin is an energy-requiring process that bacteria do when they are stressed (Fig. 6).

MFC has also employed thicker cell walls including microorganisms such as gram-positive bacteria like *Bacillus sp.* and yeast like *Pichia stipitis*. To discover key mediators in extracellular electron transport, researchers studied exoelectrogenic *Bacillus sp.* WS-XY1 and *P. stipitis*. Both bacteria employ flavins to mediate extracellular electron transport, according to the findings [34, 113].

The processes by which electrically active bacteria get electrons from the cathode are far less well understood than the processes by which similar bacteria get electrons from the anode. Nonetheless, it has been proven that bacteria get electrons from the cathode via a different process than electron transport to the anode. The *S. oneidensis* MR-1 employed riboflavin as an endogenous electron shuttle to transmit electrons to Cr(VI) inside the cathode (in the existence of lactate in aerobic states) [163]. Two methods have been documented for accepting electrons from the cathode: direct and indirect electron transfer. Electroactive microbes are in direct bodily interaction with the surface of the cathode in direct electron transfer, and electrons are accepted utilising OM c-Cysts. Indirect electron transfer, on the other hand, happens through soluble electron shuttle mediators, in which an oxidised mediator molecule is reduced to the cathode surface. Furthermore, electrons are transported to the bacteria via reduced mediator molecules [80]. A gene involved in electron transport from the cathode has been identified. A research found that the GSU2374 gene was expressed in cathodic biofilm. This gene is thought to code for a monohaem-c-type cytochrome (PccH). Moreover, mutation analysis has shown that biofilms that lack this gene are unable to absorb electrons from the cathode. Despite this, biofilms continue to contribute electrons when employed on the anode, indicating the gene's critical function in electron transfer mechanism from the cathode to the microorganisms [131].

7 Merits and Scopes of MFCs Biosensors

Enzymes are the most often utilised biological sensing component in biosensor manufacturing. Due to the time-consuming, labour-intensive and expensive process of enzyme purification, purified enzymes are not a good alternative for biosensor development. In a traditional biosensor, several enzymes are required to produce the detectable product of the cofactor/coenzyme, whereas microorganisms (MFCs) provide an excellent alternative. Because the cell has a high number of enzymes and co-factors, it can digest and detect huge amounts of substances, but this might impair selectivity. MFCs may be readily controlled and altered to consume/degrade novel substrates under culture conditions. Furthermore, advances in recombinant DNA technology have opened up more options for modifying microorganisms to increase enzyme performance, making microbes an effective biosensing element [85].

MFC has the potential to be used for sustainable effluent treatment, as well as concurrent power generation from renewable biomass and biosensing. MFC can cope with a wide range of waste streams, including industrial, agricultural and municipal wastewaters [30, 78]. The current generation now includes stackable MFCs. Erable

et al. [52] conducted research throughout the world to enhance the energy density of MFCs and get them more cost-effective to deploy on a broad scale. MFC may be utilised for a range of applications besides to wastewater treatment, such as BOD biosensors and bacterial account. As a BOD and toxicity detection biosensor, MFC enhanced with electrochemically active microbes have been employed. Toxic chemicals including arsenic, cadmium, lead, chromium (VI), mercury, surfactant, cyanide and organophosphorus compounds induce changes in the electric current signals of MFCs, making toxicity in the water simpler to detect. Current generation was shown to be relational to the concentration of hazardous and biodegradable waste at low concentrations. To examine the condition of wastewater, hazardous chemicals in the aqueous system might be combined with BOD measurements [110]. Sediment-based MFCs have recently showed potential in the management of artificial wetlands. The current generated by the sediment MFC may be stored in capacitors and then utilised to power remote sensors via a power management system. The underwater monitoring devices were designed to be powered by a solid-phase MFC. Low-power biomedical devices implanted in people have also been found to benefit from MFCs for supplying long-term, steady power [16]. The *Saccharomyces cerevisiae*-biocatalysed micro-MFCs may generate energy from glucose in the bloodstream. This MFC can be used to track food spoiling. As a result, the current generation has been revealed to be rising at a faster rate with an escalating extent of contamination. This type of technology might potentially be useful for quickly detecting and counting bacteria in contaminated food [30].

Finally, the most significant benefit of an MFC is that it is able to produce burning and pollution-free electricity directly from biomass organic substance, which may be used in the sensing process. Microorganisms use enzymatic processes to transform the energy held in chemical bonds in organic compounds into bioelectrical energy in an MFC. As a result, MFC energy production is linked to bacteria's regular life activities [101].

8 Analytical Applications of MFC-Based Biosensors

Various variables, such as organic chemical modes, pH, temperature, toxicants, inhibitors and concentration, have an impact on MFC voltage and power output. This implies that, in addition to acting as a backup power supply for remote sensors, MFCs may also be employed as biosensors to find a variety of factors [169] described below. The capacity of MFCs to produce electrical current, as well as their ability to facilitate on the spot and real-time checking of different analytes, might allow them to function as efficient biosensors. We recapped the most recent advancements in numerous biosensor applications utilising MFCs including analysing BOD, detection of toxicants and DO, monitoring microbial activity, detection of microbial biofilms and VFA, which are very significant factors for usable water.

8.1 BOD Detection

The quantity of DO required by aerobic bio-organisms to break down organic substances accessible in a given water sample at a particular temperature during a certain period is referred to as BOD. Because it serves as an indicator for evaluating the effect of discharged waste on the ecosystem, BOD is an important water quality metric [79]. The greater the BOD number, the more organic matter or food available for oxygen-consuming bacteria. Unfavourable circumstances arise when the amount of DO intake by bacteria surpasses the amount of DO supply by aquatic organisms or diffused from the air. Reduction of DO puts aquatic creatures under stress, putting the habitat unfit for existence. Furthermore, severe depletion might result in hypoxia or anoxia. BOD is also widely utilised in wastewater treatment, where the breakdown of organic waste by microbes is a typical treatment method. In general, for direct environmental wastewater discharge, the maximum permitted concentration is approximately 10 mg/L BOD, whereas for sewer system discharge, the maximum allowable concentration is around 300 mg/L BOD [129].

The amount of biodegradable material in water, or BOD, is a common element in managing and evaluating the operation of a wastewater treatment facility. The conventional method of determining BOD takes 5–7 days and should only be done by professionals. Because this approach is labour-intensive and time-consuming, an alternate method for monitoring BOD onsite that is quick and easy is required. For the first time [69], suggested the usage of MFCs as a BOD sensor. The bacterium, *Clostridium butyricum,* was immobilised on the electrode surface in the anodic compartment, and a linear correlation was detected within current output from the MFC and BOD concentration, indicating that MFC-based BOD biosensors are feasible.

Following then, some kinds of MFC-based BOD sensors were described, as well as numerous microorganisms were employed [149, 172]. MFCs with electron mediators were also investigated as BOD biosensors [152], with the mediators assisting electron transfer from the microbial cells towards the electrode, however these biosensors were unstable over time due to the toxicity of the mediators to microbes. Chang et al. [31] demonstrated that a mediatorless MFC may be utilised to constantly assess the BOD of effluent for real-time examining using a mediatorless MFC. Furthermore, an MFC-based biosensor was described to have functioned in a stable manner for over 5 years [72], which was far longer than formerly stated BOD biosensors (7–140 days) [91]. This proved the benefits of MFC-based biosensors in the long run. Unlike traditional sensors, MFC-based biosensors directly employ the quantified voltage or current as output signals, making them easier to process and display. They may also be developed and used in distant places due to their capacity to generate electricity on their own [43].

Microbial decomposition of organic substances and their transformation into an electrical current were used to develop MFC-based BOD sensors [107]. One of these BOD biosensors was made as a low-cost, single-compartment MFC utilising anodic organic substrate and activated slurry, and its viability as an actual BOD

monitoring device was confirmed [168]. When combined with synthetic wastewater, this system showed a constant voltage after 132 min, causing in a BOD rate of 200 mg/L. The response signal was observed to be enhanced and related to the trend of the increase in BOD content from 5 to 200 mg/L. After the BOD concentration exceeded 120 mg/L, the response signal remained constant. To address several of the constraints of the MFC-based BOD biosensor, a novel arrangement with enhanced features was designed, which used an exterior voltage to surmount internal resistance and permit microorganisms to amplify electricity generation [107]. This configuration was membrane-free to avoid pH fluctuations that would limit the sensor's applicability to low alkaline effluents. During a 20 h reaction period, BOD levels ranging from 32 to 1280 mg/L showed a linear relationship with charge. The sensing ability was lowered to a level of BOD of up to 320 mg/L when the response period was cut to 5 h. The need of exterior voltage equipment for MFC biosensors limits their use to remote monitoring in far-flung locales. Auto-generated power floating biosensors for actual water condition checking were developed as a result, removing the requirement for external power and allowing maintenance to be incorporated into other settings [123].

BOD sensors, on the other hand, are employed in the early detection of feed water condition. This technique is valuable for detecting the beginning of biofouling in reverse osmosis (RO) membranes used in saltwater purification [128].

Biofouling is one of the most severe troubles in desalination techniques, since it causes serious problems such as flux loss, short membrane lifetime and increased energy usage. Before starting the RO process, recent biofouling detection methods measure the silt total direct cell quantification [64], density index [9] and the biofilm growth rate [77].

As a result, detecting assimilable organic carbon (AOC) in the feed flow of RO plants is a useful method for estimating possible biofouling. AOC monitoring marine MFC biosensors was built, injected with a marine sediment bacterial strain, and examined for 36 days. In the range of 0–150 μmol/L (0–3600 μg/L) of AOC, the results indicated a linear connection between electrochemical signals and acetate concentration. Nonetheless, at high acetate concentrations ranging from 150 to 450 μmol/L (3600–10,800 μg/L) of AOC, this biosensor revealed a deviating linear relationship [49].

8.2 Toxicity Detection

The industrial revolution advances civilization, but it also introduces a plethora of new-to-nature compounds into the environment including water [124]. Many of them are hazardous to both people and other living things. The detection of toxicity in water is a key criterion in identifying the measures that must be taken to provide safe, high-quality water for human, animal and agricultural use. Off-site chemical analysis utilising physicochemical techniques such as high-performance liquid chromatography, gas chromatography-mass spectrometry and mass spectrometry is a

traditional strategy [38, 61]. These techniques are often slow and ineffective for real-time detection. MFC-based biosensors are an excellent option since they are directly based on the toxicants' biotoxicity impacts. The composition of wastewater can be quite complicated, and a wide range of poisonous substance may be available. Compounds that can change the pH of wastewater, such as acid mine drainage, where the pH can be down to 2.4, inorganic and organic compounds with extremely severe toxic properties, phenolic compounds, heavy metals and so on, are all potential toxicants [141]. Toxic contaminants can block the action of electrogens, causing the current produced by MFCs to be interrupted [74]. The current diminishes the more poisonous the chemical is to the bacteria. As a result, multiple toxicity sensors may be developed based on the connection between hazardous chemicals and current decrease amplitude [169]. Toxicity sensors are primarily utilised to evaluate if the concentration of hazardous chemicals in an effluent surpasses the regulatory highest concentration limit. As a result, the emphasis of MFC biosensor for toxicity testing is based on the detection limit of the contaminants rather than the linear range as in BOD. The detection threshold of MFC-based toxicity biosensors is yet far away from the World Health Organization's water quality standard (tens to hundreds of times higher) [67]. Heavy metals sensors, antibiotics detection sensors, organic toxicants sensors and acidic toxicity sensors are the four main types of MFC-based toxicity biosensors depending on the target pollutants.

Heavy metals detection

Pollution containing heavy metals has the potential to harm human health as well as the environment. Heavy metals, such as mercury and arsenic, for example, produce significant toxicity in the neurons and endocrine system, as well as heart problems, skin damage and cancer [61]. Heavy metallic elements have a lengthy half-life (ten to hundreds of years) and are difficult for microbes to eliminate or decrease. They will also accumulate in the human body as they go up the food chain, and once certain concentrations are reached, they may cause health issues, despite the fact that some of them are necessary for human health [151].

Heavy metal ions can limit microorganisms' respiration activities [57], which is the basis for affecting the current generation of MFCs. Six heavy metals such as Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+} and Pb^{2+}ions (2 mg/L) were evaluated in a double compartment MFC arrangement, and their resistant rates on current output were 12.56%, 13.99%, 8.81%, 9.29%, 5.59% and 1.95%, respectively [175]. Zhiheng [167] proposed a flat membrane-based MFC biosensor and verified it with two different ions (Ni^{2+} and Cr^{6+}) to increase the sensitivity and stability of MFC-based biosensors. After adding 10 mg/L Cr^{6+} for 40 min, the voltage dropped to 40 mV from 180 mV, and after adding 20 mg/L Cr^{6+}, the voltage dropped to 50 mV in 6 min. Injecting Ni^{2+} (20 mg/L) into the anolyte, on the other hand, only caused in a modest voltage decrease from 180 to 150 mV after 180 min. With a higher concentration (50 mg/L Ni^{2+}), the voltage decrease occurred faster (45 min), but the change was in the same range.

Heavy metallic ions can compete for electrons with the anode in the anodic compartment, resulting in a small number of electrons being transported to the

cathode in some MFCs designed for specific target compounds. Cr^{6+} is a terminal electron acceptor that may be reduced by Cr^{6+}-reducing anaerobes in anaerobic circumstances [37]. When an MFC is made utilising Cr^{6+}-reducing anaerobes, the cell voltage is anticipated to drop as the Cr^{6+} concentration rises. The Cr^{6+}-reducing bacterium *Ochrobactrum anthropi* YC152 was injected into an MFC for the determination of Cr^{6+} as proof of concept (Guey-Horng [156]). The outcomes showed that the proposed biosensor can detect Cr^{6+} in the scale of 0.0125–5 mg/L quantitatively. Wu et al. established a comparable method utilising *Exiguobacterium aestuarii* YC211, a Cr^{6+}-reducing bacteria with a linear range of 2.5–60 mg/L [160].

In contrast to the negative effects, there was also a positive connection between ions and MFC outputs. Iron-oxidising bacteria were a good example. Iron-oxidising bacterial consortia can employ iron (II) as the only electron source in the Anolyte. To build an MFC-based biosensor [153], injected this particular bacterial community onto the anode. Within the concentration range of 3–20 mM, a linear relationship between current output and Fe^{2+} was found.

Rather than detecting heavy metallic ions through their biological effects on electrogens, the biosensor may be constructed by using them as MFC cathode electron acceptors. In MFC sensors, the abiotic cathode-sensing element has recently been explored to detect heavy metallic ions (e.g. Cu^{2+}, Cr^{6+}). Shuai Zhao et al. [182] applied a sediment MFC (SMFC) to watch Cr^{6+} in industrial effluent and found that Cr^{6+} was decreased at the cathode. The linear response scale was 0.2–0.7 mg/L, which was significant for Cr^{6+} detection limit. The Cu^{2+}, which acts as an electron acceptor and is finally accumulated on the surface of cathode as Cu (0), was also measured using the SMFC [161]. The voltage increases and the Cu^{2+} intensity (5–160 mg/L) was found to have a linear relationship ($R^2 = 0.87$).

Heavy metallic ions in tap water are now monitored using MFC-based biosensors. In order to detect toxic shocks in tap water, an MFC biosensor based on O_2-reducing bacterial cathodes was developed [127]. The detection limits for three heavy metallic ions (Cr^{6+}, Hg^{2+} and Pb^{2+}) were found to be in the range of 1–10 mg/L.

Antibiotics detection

Antibiotics are utilised in animal production, as a preventative measure in animal feed, and as therapeutic medicines. Only a tiny percentage of antibiotics consumed by fauna are metabolised, allowing a large part to accumulate in tissues or be excreted and released into the environment. Antibiotics in the environment may lead to antibiotic resistance, with the risk of transmission to humans via the food chain [61]. Antibiotics have saved millions of lives, but their inappropriate management and release into the environment has disrupted the normal evolution process, posing several safety concerns for microbial ecosystems and, as a result, humans [59]. Tracing and controlling antibiotic discharge and distribution has become a critical issue for future generations. MFC is one of the real-time techniques for detecting antibiotics in the field, among all the antibiotic sensors.

To detect tobramycin, Wenguo [162] built a single-chamber MFC with hydrophilic carbon fabric as the anode. There were no discernible effects at concentrations of 0.10, 0.24 and 0.47 g/L. However, as the concentration reached 0.93 g/L or above, the

current production dropped significantly. After the addition of tobramycin, less than half of the initial current production could be preserved. Interestingly, depending on the tobramycin concentration, the current might be restored after hundreds of hours. Owing to the 'self-healing' nature of the electroactive biofilms in MFCs, this occurrence indicates the stability of MFC-based sensors for tobramycin (and perhaps other antibiotics) detection over long-term operation.

Schneider et al. [135] used tiny MFCs in a panel system to develop a rapid method to β-lactam antibiotics analysis. Two model bacteria, *E. coli* strain ATCC 25,922 and *S. aureus* strain ATCC 29,213, were employed to test hypothesis proof, and 10 separate β-lactam antibiotics (cefoxitin, ampicillin, cefazolin, cefoperazone, cefepime, cefuroxime, imipenem, ticarcillin and penicillin) were tested at concentrations varying from 1 to 75 μg/mL. 2–4 h after introducing the cell mix solution into the MFCs, the antibiologic effects of these drugs could be evaluated in terms of changes in cell voltage output, whereas the standard Kirby–Bauer disc diffusion technique for antibiotic testing needs 24–48 h.

A single-chamber MFC was utilised to test another frequently used antibiotic, levofloxacin [177]. The MFC biosensor can identify levofloxacin at up to 1000 μg/L using sodium acetate as the energy source in the anode. In the range of 0.1–100 μg/L, a linear association ($R^2 = 0.924$) was found between current yield and levofloxacin antibiotic concentration. Furthermore, this MFC has been operational for over 14 months and continues to generate a consistent electrical production, illustrating the benefits of MFC-based biosensors for antibiotic detection in enduring usage.

Organic Toxicants detection

Organic toxicants in water, such as polycyclic aromatic hydrocarbons, organic phosphate compounds, organic nitrogen compounds and polychlorinated biphenyls (PCBs), can induce eutrophication and have negative consequences for public safety [83, 137, 170]. Kim et al. [74] used a double-chamber MFC to investigate the toxicity of diazinon and PCBs, finding inhibition of 61% and 38%, respectively, for diazinon and PCBs (1 mg/L). Weiyang Yang et al. [171] established a special micro-sized MFC for formaldehyde detection in water. A solid-state thin film Ag/AgCl reference electrode and a microscale air bubble trap were used in this micro-sized system to maintain an optimum anodic potential and counteract microscale air bubbles from accessing the MFC biosensor. The current dropped proportionately to the concentration of formaldehyde in the medium, which ranged from 0.001 to 0.10%, whereas the anode voltage was held constant at 0.20 V versus the reference electrode. A single-element paper MFC has recently been developed and tested for chemical detection in the water phase [39]. During the procedure, the recyclable carbon-based electrodes were imprinted on a single sheet of paper, with the anode merging into the liquid state and the cathode remaining in the gas phase. Because of the capillary force generated by the paper material, the paper basement served as both a divider between electrodes and a bridge for mass transfer. The addition of 0.1% (v/v) formaldehyde to the existing output resulted in an abrupt decrease in the current production. Furthermore, two MFCs may be printed on a single sheet of paper and linked in parallel by folding

them back to back. The current output of the stacked MFCs was entirely dropped in 115 min, contrasted to 175 min for the single paper MFC, indicating that they were more sensitive to formaldehyde shock.

In contrast to the inhibitory impacts, Zhengjun [36] developed a double-chamber MFC utilising p-nitrophenol (PNP) as the only substrate that exhibits stimulatory effects. The anodic chamber was kept in an aerobic state by inoculating the reactor with an aerobic bacterium, *Pseudomonas monteilii* LZU-3. The cell voltage improved at higher PNP concentrations when the optimum operating parameters were used (pH of 7.8, external resistance of 1000 W and temperature of 30 °C). The PNP concentrations in the range of 16–44 mg/L were found to have the highest linear voltage relationship ($R^2 = 0.98$). Even when PNP was combined with other aromatic molecules (5 mg/L of toluene, nitrobenzene and 2-nitrophenol), a linear relationship between PNP concentrations (9–36 mg/L) and cell voltage could be seen.

Acidic Toxicity detection

Acidic toxicity is of particular importance to be checked online, since numerous forms of hazardous chemicals in wastewater, such as mine drainage, induce a rapid shift in pH [148]. A low pH value inhibits microbial growth and activity and inhibits the growth of other aquatic plants and animals, reducing the water body's capacity to self-purify and deteriorating the water quality. A single-compartment air-cathode MFC was constructed and functioned in a continuous batch method by Yu et al. [141]. HCl was used to change the pH of the influent (i.e. the electrolyte in the working compartment). When the pH was kept within 3–4, the output voltage dropped quickly and then retrieved after the addition of HCl was stopped. Altering the pH of the influent to a value of 2, on the other hand, resulted in a voltage output crisis, which was most likely triggered by the total destruction of electrochemically active biofilm in high acidic circumstances. To detect acidic toxicity, [66] built a cathode shared MFC sensor arrangement. Because the cathode performance fluctuation was minimised, the detection credibility of this sensor assembly operating in non-stop mode might be guaranteed. After the MFC array attained a steady state, acidified anolyte was used to provide an acidic toxicity shock. The voltage dropped from 200 to 0 mV very quickly when the pH was lowered from 6 to 4. The threshold value of pH may vary depending on the biofilm composition, nonetheless, this phenomenon allows for a possible method of obtaining the pH in water, based on the disruption of MFC cell voltage.

Acid rain impact was also reported to be observed, likewise, to checking acidic toxicity in water. Rhizosphere microorganisms in plant MFCs (PMFCs) may produce electrical current by decomposing the organic defaecates of the rhizodeposits, thus any variations in the bioavailable substrate concentration could impact the electrical current [134]. Tian [86] used a mixture of concentrated HNO_3 and H_2SO_4 solution to imitate acid rain and built PMFCs to assess acid rain damage. Artificial acid rain might harm rice plant leaves, lowering photosynthetic activity, which is linked to rhizospheric electrochemical activity. After pretended acid rain was sprayed on the leaves of plant, immediate and reproducible current decrease was recorded within 2 min, which was in good agreement with variations in rhizospheric organic concentration.

8.3 DO Detection

In natural waterways, oxygen is required for a variety of chemical, biological and metabolic processes. DO is without a doubt one of the most important and broadly used indicators of water quality [180]. The levels of DO in aquatic settings provide an essential quality indicator for biochemical and biological activities. To detect DO in water, various physical, chemical and electrochemical techniques have been developed [35]. Though electrochemical techniques are widely utilised due to their ease of application and high sensitivity, the biological applications of these technologies have been studied in a few research. The development of a submergible MFC biosensor for online and in situ quantification of DO in aquatic environments was one of the first efforts to employ a bioelectrochemical sensor for DO [180]. The sensor was powered using domestic effluent as a substrate. The functioning of the sensor was evaluated using tap water as a control at various DO concentrations. When employing an external resistance of 1000, the sensor produced a current intensity in the range of 5·60–462·20 mA/m^2; as a result, it linearly rose with the increase of DO intensity up to 8.80 mg/L, with a reaction time of below 4 min for each measurement [49].

The quantity of dissolved oxygen (DO) in water is an important indication and a frequent criterion in water management [102]. Its fluctuations, for example, have been found to correlate the amount of organic contaminants flowing into a freshwater lake [11]. It also offers crucial information on biological and metabolic processes in the water ecosystem, and the DO level acts as a natural selecting pressure for various microbe lifestyles. Because Clark-type oxygen sensors are substantially influenced by ambient factors such as pressure, reliable DO measurement in the field is difficult [102]. MFCs are an alternate method for measuring DO. MFC-based biosensors are more robust against external conditions than Clark-type oxygen electrodes and can enable actual checking in the field. The cathode behaviour is the core concept of MFC-based DO measurement. The cathode efficiency is a performance limitation for MFCs [181] but oxygen, as the ultimate electron acceptor, has a substantial impact on the cathodic reduction rate and therefore the current output. Oh et al. [115] discovered a Monod-like kinetic connection between DO levels and current density, with a 1.74 mg/L half saturated DO value.

The ability to measure DO online can be useful for understanding the aquatic ecology. Periodic oxygen stratification has been discovered in several shallow freshwater nutrient enriched lakes in recent years, which ultimately leads to the creation of a lake's 'dead zone' [139, 179]. Monitoring DO levels in a lake can act as a primary warning system for the possibility of a 'dead zone'. Song et al. developed a sediment-based multiple cathode MFC system for this purpose, which incorporates several cathodes positioned at various depths of water for in situ, non-stop and online monitoring of DO intensities and lake deepness [144, 145]. In the range of 0.0–9.0 mg/L, there was a direct connection ($R^2 = 0.9576$) between voltage and DO [144, 145].

8.4 Microbial Activity Detection

Because the presence of *Escherichia coli* indicates faecal contamination, a precise quantification of *E. coli* can be regarded critical for detecting faecal contamination and safeguarding community health. An MFC was employed as an *E. coli* sensor, with specified *E. coli* enzymes, for instance, β-d-glucuronidase (GUS) and β-d-galactosidase (GAL) serving as biological monitoring components [76]. The GUS was measured using 4-nitrophenyl-β-d glucuronide and 8-hydroxyquinoline glucuronide as substrates, whereas GAL was measured using 4-aminophenyl β-d-galactopyranoside as a substrate. The detection process of these compounds is based on GUS or GAL hydrolysis, followed by electrochemical activation and an oxidation phase in the MFC's anode compartment. As the *E. coli* concentration approached the threshold level, the power produced by the MFC reactor increased dramatically [49].

Microorganism screening and phenotyping using traditional microbiological methods are quantitative but labour-intensive and time-consuming. MFC was recommended in this context as a quick and simple way to get first-hand information about the microbe and its overall lifestyle [3]. The process is based on microbial metabolic activity (and hence electron output to anode) that is uniquely influenced by the surrounding environmental conditions. Miller and Oremland [104] reported a study that used arsenate's ability to function as an anode for electrons to predict the existence of arsenate-respiring microbes in soda lakes. Abrevaya et al. [1] presented another hypothetical application: using MFC to identify live (micro) organisms on distant planets, provided they might likewise export electrons throughout their life process. An MFC has been demonstrated to be a suitable technique for bioprocess monitoring in more practical terms. Zhidan Liu et al. [93] used a flow-cell MFC to track anaerobic digestor functioning and discovered that current production variations were connected to fluctuations in working indicators such as pH, gas flow rate and COD. Furthermore, MFC current density was linear for acetate intensity up to 20 mM, according to Zhidan Liu et al. [93], with very little interference from other volatile fatty acids available in the anaerobic digestor. These findings suggested that an MFC-based biosensor might be used to monitor the anaerobic digestor's metabolic turnover rates of organic molecules.

8.5 Monitoring of the Corrosive Biofilms

In several industries, such as the gas and oil industry and water utilities, microbiologically induced corrosion (MIC) is a key concern [165]. According to [8], MIC is responsible for 20% of all corrosion damage. Microbial biofilms, particularly anaerobic bacteria, are the major source of MIC owing to their metabolic activity or metabolites. Most anaerobic MIC attacks fall into one of two categories: respiration or fermentation. Microorganisms that undertake anaerobic respiration are included

in Type-I MIC. Sulphate is the terminal electron acceptor in respiration of Sulphate-Reducing Bactria (SRB). As electron donors, organic compounds such as volatile fatty acids are frequently employed. Type-II MIC is characterised by the secretion of caustic metabolic products such as organic acids. Because biocorrosion is usually accompanied by a low pH, it is easy to detect. Because oxygen is cut off to prevent extreme corrosion of carbon steel, gas and oil pipelines are always maintained anaerobic. The cathodic biofilm is fed by electrons from a solid-state anode. If a corrosive biofilm is formed to the cathode, such as SRB biofilm, the electrogenic biofilm will transport the biofilm to the cytol of sessile cells, reducing sulphate levels [164].

The ability to recognise corrosive biofilms is critical when deciding whether to employ biocides or mechanical pigs to combat them. Available biofilm sensors measure electrical resistance variations across a biofilm by applying an external electrical field. This, however, disrupts the biofilm metabolism. In addition, because these sensors cannot tell the difference between a mineral layer and a biofilm, a passive sensor that does not require an exterior voltage is preferred to avoid misleading findings [169].

Electrogenicity was presented by Gu [60] as a sign of the existence of a corrosive biofilm and their potential to attack metal. The cathodic biofilm is fed by electrons from a solid-state anode. If a corrosive biofilm attaches to the cathode, like an SRB biofilm, the electrogenic biofilm will transport the biofilm to the cytol of sessile cells, reducing sulphate [164]. After calibration, the open-circuit voltage can be utilised to determine if nitrate reduction, sulphate reduction or other chemical reactions are happening at the cathode. The capacity of the cathodic biofilm to transfer extracellular electrons, which is a deadlock for an electrogenic biofilm to biocorrode, is measured by closed-circuit current flow [178].

8.6 Volatile Fatty Acids (VFA) Detection

VFAs must be monitored closely in anaerobic digesters since their aggregation can cause pH decrease and reactor failure. VFAs are often tested offline using high-pressure liquid chromatography or gas chromatography, for example, pH titration [53] and headspace gas chromatography [20] are two online methods that can identify specific VFAs but need costly equipment.

VFA sensors have also been studied using microbial electrochemical systems. Acetate is a frequent substrate in MFC research, and biological anodes have already been demonstrated to convert other VFAs into electrical current [56, 90]. MFCs were enhanced with butyrate propionate and acetate, by Kaur et al. [70]. They used cyclic voltammetry to examine the response and discovered correlation between peak current and VFA concentration. Surprisingly, MFCs enhanced in acetate and propionate only responded electrochemically when fed with their respective substrates, but MFCs enriched in butyrate responded to all substrates. This implies that acetate or propionate-specific microbial electrochemical biosensors could be possible to

develop. This is especially important since the ratio of propionate to acetate concentration is a critical process parameter whose rapid shift can serve as an early warning sign of anaerobic digester problems. It should be emphasised that in an anaerobic digester, maintaining electroactive microbial populations specialised to acetate or propionate is likely to be challenging. Using membranes that prevent pre-enriched biofilms from invasion by other species while allowing substrate transfer might be a strategy to preserve the biosensor's substrate specificity.

9 Challenges and Perspectives

The MFC-based biosensor has gained increasing attention as an analytical technique due to the use of whole cells and self-powering capability. Significant advances have been achieved in the field, particularly in the detection of toxicity and BOD. However, several issues must be resolved before it can be considered a mature sensing technology that is recognised by scientific communities and stakeholders.

First, additional research into the stability of MFC-based biosensors is urgently needed, as it is frequently ignored. MFC employs a self-renewable catalyst in the form of microorganisms. During long-term operation, bacteria can grow quickly in response to ecological alterations. As a result, the biosensors' sensitivity, selectivity and repeatability may be compromised.

The limit of detection of MFC-based biosensors, particularly for toxicity measurement, is generally much lower than the World Health Organization's water quality standard. A promising method for improving MFC-based biosensors could be to screen bacteria with a high extracellular electron transfer rate. Creating genetically modified microbes might potentially be an option for improving biosensor performance. The discovery of electrogenic genes linked to electron transport and metabolism broadens the possibilities of MFC-based biosensors, allowing them to be used for different types of applications.

Furthermore, because water quality has a significant impact on the electric signal yield of MFC-based biosensors, intervention of signal may emerge, particularly in intricate aquatic settings. A change in BOD, for example, can mute the signal for toxic substances. Jiang et al. [65] investigated the impact of background organic material content on the functioning of MFC-based toxicity biosensors in a systematic way. They evaluated the signal output of two MFC biosensors with low and high organic material contents to a pre-made response chart to produce qualitative distinctions in order to prevent signal intervention in the collective shock of toxicity and BOD. To prevent the mutual shock of toxicity and BOD, Jiang et al. [66] used biocathode for toxicity examining. Majority of MFC-based toxicity biosensors can only measure overall toxicity, and just a few research looked at the toxicity of a specific agent. *Pseudomonas monteilii* LZU-3, used to detect PNP, is an example of a pure cultivated or genetically modified bacterium that may be utilised in MFC-based biosensors for

specialised monitoring [36]. A multi-chamber MFC biosensor with distinct electrogenic microorganisms inoculated in each chamber was also constructed to detect distinct target toxic materials in the same flow [24].

Many recent research has focused on MFC system assimilation, such as the combination of multiple anode or cathode or multiple cell MFCs, combined with other chemical or physical processes, and extending MFCs with other biological methods to increase the operating performance of MFC. When compared to a single anode/cathode, these configurations can achieve better power density [46]. However, improving the selectivity of MFC-based biosensors remains a major issue. As a result, additional research using molecular biology or other contemporary approaches is needed to improve specificity and sensitivity.

10 Conclusions

Microbial fuel cells (MFCs) have appeared as the next viable and environmentally benign energy source and, over the last two decades, MFC-based biosensors have advanced at a breakneck pace as an analytical tool. MFCs-based biosensors are gaining popularity in various fields due to their ease of application and long-term viability in quality monitoring of the environment. These biosensors are often low cost, self-powered and capable of real-time remote monitoring. It also offers distinct advantages in many applications, including ease of fabrication, ease of operation, economical and in situ monitoring. MFC-based biosensors may become recognised as standard techniques. These biosensors are built on the activity of microbes in MFCs. They can transmit electrons directly through their outer membrane proteins or pili overlaying the bacterium's outer surface. MFC technology is a unique way of utilising bacteria to generate bioelectricity from organic waste and renewable biomass using the redox metabolic processes of microorganisms. They can detect characteristics and events in their environment and transform that information into signals. MFC-based biosensors have a lot of possibility for monitoring BOD, hazardous chemicals, DO, corrosive biofilm presence and corrosivity, microbial activity analysis, VFA and anaerobic digester performance or as an energy source for other sensors.

The capacity of MFCs to produce electrical current, as well as their ability to facilitate on the spot and real-time testing of different analytes, might allow them to function as efficient sensors. But till there are limitations and lots of scope available for further development to make them viable and perfect for analytical applications. A better understanding of biofilm characteristics and organism genetic manipulation might lead to novel ways to enhance the performance of MFC-based biosensors. Some of them may see actual deployment in the near future. Majority of biosensors function well in the lab but need to be tweaked for use in the field.

References

1. Abrevaya XC, Mauas PJ, Cortón E (2010) Microbial fuel cells applied to the metabolically based detection of extraterrestrial life. Astrobiology 10(10):965–971
2. Abrevaya XC, Sacco NJ, Bonetto MC, Hilding-Ohlsson A, Cortón E (2015a) Analytical applications of microbial fuel cells. Part I: biochemical oxygen demand. Biosens Bioelectron 63:580–590
3. Abrevaya XC, Sacco NJ, Bonetto MC, Hilding-Ohlsson A, Cortón E (2015) Analytical applications of microbial fuel cells. Part II: toxicity, microbial activity and quantification, single analyte detection and other uses. Biosens Bioelectron 63:591–601
4. Adhikari RY, Malvankar NS, Tuominen MT, Lovley DR (2016) Conductivity of individual Geobacter pili. RSC Adv 6(10):8354–8357
5. Aghababaie M, Farhadian M, Jeihanipour A, Biria D (2015) Effective factors on the performance of microbial fuel cells in wastewater treatment—A review. Environ Technol Rev 4(1):71–89
6. Agubra V, Fergus J (2013) Lithium ion battery anode aging mechanisms. Materials 6(4):1310–1325
7. AKim H, Park H, Hyun M (2002) A media-tor less microbial fuel cell using a metal reducing bacte-rium, Shewanella putrefaciense. Enzyme Microb Technol 30(2):145–152
8. AlAbbas FM, Williamson C, Bhola SM, Spear JR, Olson DL, Mishra B et al (2013) Influence of sulfate reducing bacterial biofilm on corrosion behavior of low-alloy, high-strength steel (API-5L X80). Int Biodeter Biodegrad 78:34–42
9. Alhadidi A, Kemperman A, Blankert B, Schippers J, Wessling M, Van der Meer W (2011) Silt density index and modified fouling index relation, and effect of pressure, temperature and membrane resistance. Desalination 273(1):48–56
10. Angelaalincy MJ, Navanietha Krishnaraj R, Shakambari G, Ashokkumar B, Kathiresan S, Varalakshmi P (2018) Biofilm engineering approaches for improving the performance of microbial fuel cells and bioelectrochemical systems. Front Energy Res 6:63
11. Ansa-Asare O, Marr I, Cresser M (2000) Evaluation of modelled and measured patterns of dissolved oxygen in a freshwater lake as an indicator of the presence of biodegradable organic pollution. Water Res 34(4):1079–1088
12. Anu Prathap M, Chaurasia AK, Sawant SN, Apte S (2012) Polyaniline-based highly sensitive microbial biosensor for selective detection of lindane. Anal Chem 84(15):6672–6678
13. Asensio Y, Montes I, Fernandez-Marchante C, Lobato J, Cañizares P, Rodrigo M (2017) Selection of cheap electrodes for two-compartment microbial fuel cells. J Electroanal Chem 785:235–240
14. Askari A, Vahabzadeh F, Mardanpour MM (2021) Quantitative determination of linear alkylbenzene sulfonate (LAS) concentration and simultaneous power generation in a microbial fuel cell-based biosensor. J Clean Prod 294:126349
15. Asim AY, Mohamad N, Khalid U, Tabassum P, Akil A, Lokhat D, Siti H (2021) A glimpse into the microbial fuel cells for wastewater treatment with energy generation. Desalin Water Treat 214:379–389
16. Babauta J, Renslow R, Lewandowski Z, Beyenal H (2012) Electrochemically active biofilms: facts and fiction A review. Biofouling 28(8):789–812
17. Barua E, Hossain MS, Shaha M, Islam E, Zohora FT, Protity AT et al (2018) Generation of electricity using microbial fuel cell (MFC) from sludge. Bangladesh J Microbiol 35(1):23–26
18. Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi SV, Pavlostathis SG, Rozzi A et al (2002) The IWA anaerobic digestion model no 1 (ADM1). Water Sci Technol 45(10):65–73
19. Beylier MR, Balaguer M, Colprim J, Pellicer-Nàcher C, Ni B, Smets B et al (2011) 6.27-Biological nitrogen removal from domestic wastewater. Compr Biotechnol 6:329–340
20. Boe K, Batstone DJ, Angelidaki I (2007) An innovative online VFA monitoring system for the anerobic process, based on headspace gas chromatography. Biotechnol Bioeng 96(4):712–721
21. Bond DR, Lovley DR (2003) Electricity production by geobacter sulfurreducens attached to electrodes. Appl Environ Microbiol 69(3):1548–1555

22. Boyle D, Magno M, O'Flynn B, Brunelli D, Popovici E, Benini L (2011) Towards persistent structural health monitoring through sustainable wireless sensor networks. In: 2011 seventh international conference on intelligent sensors, sensor networks and information processing. IEEE, pp 323–328
23. Brunelli D, Tosato P, Rossi M (2016) Microbial fuel cell as a biosensor and a power source for flora health monitoring. In: 2016 IEEE sensors. IEEE, pp 1–3
24. Buck J, Silver M (2015) Microbially-based sensors for environmental monitoring. Google Patents
25. Calabrese Barton S, Gallaway J, Atanassov P (2004) Enzymatic biofuel cells for implantable and microscale devices. Chem Rev 104(10):4867–4886
26. Call D, Logan BE (2008) Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane. Environ Sci Technol 42(9):3401–3406
27. Capodaglio A, Molognoni D, Dallago E, Liberale A, Cella R, Longoni P et al (2013) Microbial fuel cells for direct electrical energy recovery from urban wastewaters. Sci World J
28. Chabert N, Ali OA, Achouak W (2015) All ecosystems potentially host electrogenic bacteria. Bioelectrochemistry 106:88–96
29. Chan AC, Ager D, Thompson IP (2013) Resolving the mechanism of bacterial inhibition by plant secondary metabolites employing a combination of whole-cell biosensors. J Microbiol Methods 93(3):209–217
30. Chandrasekhar K, Amulya K, Mohan SV (2015) Solid phase bio-electrofermentation of food waste to harvest value-added products associated with waste remediation. Waste Manag 45:57–65
31. Chang IS, Jang JK, Gil GC, Kim M, Kim HJ, Cho BW et al (2004) Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. Biosens Bioelectron 19(6):607–613
32. Chang IS, Moon H, Jang JK, Kim BH (2005) Improvement of a microbial fuel cell performance as a BOD sensor using respiratory inhibitors. Biosens Bioelectron 20(9):1856–1859
33. Chaudhuri SK, Lovley DR (2003) Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat Biotechnol 21(10):1229–1232
34. Chen S, Rotaru A-E, Liu F, Philips J, Woodard TL, Nevin KP et al (2014) Carbon cloth stimulates direct interspecies electron transfer in syntrophic co-cultures. Biores Technol 173:82–86
35. Chen Y-P, Liu S-Y, Yu H-Q (2007) A simple and rapid method for measuring dissolved oxygen in waters with gold microelectrode. Anal Chim Acta 598(2):249–253
36. Chen Z, Niu Y, Zhao S, Khan A, Ling Z, Chen Y et al (2016) A novel biosensor for p-nitrophenol based on an aerobic anode microbial fuel cell. Biosens Bioelectron 85:860–868
37. Cheung K, Gu J-D (2007) Mechanism of hexavalent chromium detoxification by microorganisms and bioremediation application potential: a review. Int Biodeter Biodegrad 59(1):8–15
38. Choi SH, Gu MB (2003) Toxicity biomonitoring of degradation byproducts using freeze-dried recombinant bioluminescent bacteria. Anal Chim Acta 481(2):229–238
39. Chouler J, Cruz-Izquierdo Á, Rengaraj S, Scott JL, Di Lorenzo M (2018) A screen-printed paper microbial fuel cell biosensor for detection of toxic compounds in water. Biosens Bioelectron 102:49–56
40. Chouler J, Di Lorenzo M (2015) Water quality monitoring in developing countries; can microbial fuel cells be the answer? Biosensors 5(3):450–470
41. Clark DP, Pazdernik NJ (2016) Chapter 12—Environmental biotechnology. In: Clark DP, Pazdernik NJ (eds) Biotechnology, 2nd edn. Academic Cell, Boston, pp 393–418. https://doi.org/10.1016/B978-0-12-385015-7.00012-0
42. Cohen B (1931) The bacterial culture as an electrical half-cell. J Bacteriol 21(1):18–19
43. Cui Y, Lai B, Tang X (2019) Microbial fuel cell-based biosensors. Biosensors 9(3):92
44. D'souza S (2001) Microbial biosensors. Biosens Bioelectron 16(6):337–353
45. Di Lorenzo M, Thomson AR, Schneider K, Cameron PJ, Ieropoulos I (2014) A small-scale air-cathode microbial fuel cell for on-line monitoring of water quality. Biosens Bioelectron 62:182–188

46. Do MH, Ngo HH, Guo W, Chang SW, Nguyen DD, Liu Y et al (2020) Microbial fuel cell-based biosensor for online monitoring wastewater quality: a critical review. Sci Total Environ 712:135612
47. Dong X, Wang P, Fang W, Su C-Y, Chen Y-H, Li L-J et al (2011) Growth of large-sized graphene thin-films by liquid precursor-based chemical vapor deposition under atmospheric pressure. Carbon 49(11):3672–3678
48. Donovan C, Dewan A, Peng H, Heo D, Beyenal H (2011) Power management system for a 2.5 W remote sensor powered by a sediment microbial fuel cell. J Power Sour 196(3):1171–1177
49. ElMekawy A, Hegab H, Pant D, Saint C (2018) Bio-analytical applications of microbial fuel cell—based biosensors for onsite water quality monitoring. J Appl Microbiol 124(1):302–313
50. ElMekawy A, Hegab HM, Dominguez-Benetton X, Pant D (2013) Internal resistance of microfluidic microbial fuel cell: challenges and potential opportunities. Biores Technol 142:672–682
51. ElMekawy A, Hegab HM, Losic D, Saint CP, Pant D (2017) Applications of graphene in microbial fuel cells: the gap between promise and reality. Renew Sustain Energy Rev 72:1389–1403
52. Erable B, Duţeanu NM, Ghangrekar MM, Dumas C, Scott K (2010) Application of electroactive biofilms. Biofouling 26(1):57–71
53. Feitkenhauer H, von Sachs J, Meyer U (2002) On-line titration of volatile fatty acids for the process control of anaerobic digestion plants. Water Res 36(1):212–218
54. Feng Y, Barr W, Harper W Jr (2013) Neural network processing of microbial fuel cell signals for the identification of chemicals present in water. J Environ Manag 120:84–92
55. Flimban SG, Ismail IM, Kim T, Oh S-E (2019) Overview of recent advancements in the microbial fuel cell from fundamentals to applications: design, major elements, and scalability. Energies 12(17):3390
56. Freguia S, Teh EH, Boon N, Leung KM, Keller J, Rabaey K (2010) Microbial fuel cells operating on mixed fatty acids. Biores Technol 101(4):1233–1238
57. Giller KE, Witter E, Mcgrath SP (1998) Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. Soil Biol Biochem 30(10–11):1389–1414
58. Gorby YA, Yanina S, McLean JS, Rosso KM, Moyles D, Dohnalkova A et al (2006) Electrically conductive bacterial nanowires produced by Shewanella oneidensis strain MR-1 and other microorganisms. Proc Natl Acad Sci 103(30):11358–11363
59. Gothwal R, Shashidhar T (2015) Antibiotic pollution in the environment: a review. Clean-Soil Air Water 43(4):479–489
60. Gu T (2012) Methods and devices for the detection of biofilms. World Intellectual Property Organization: Patent WO2012/149487
61. Hashem A, Hossain MM, Al Mamun M, Simarani K, Johan MR (2021) Nanomaterials based electrochemical nucleic acid biosensors for environmental monitoring: a review. Appl Surf Sci Adv 4:100064
62. Islam E, Hossain MS, Sarker PK, Towhid ST, Salimullah M, Hashem A (2020) Isolation and characterization of electrogenic bacteria from tannery wastewater. Bangladesh J Microbiol 37(1):23–27
63. Ivars-Barceló F, Zuliani A, Fallah M, Mashkour M, Rahimnejad M, Luque R (2018) Novel applications of microbial fuel cells in sensors and biosensors. Appl Sci 8(7):1184
64. Jeong S, Kim LH, Kim S-J, Nguyen TV, Vigneswaran S, Kim IS (2012) Biofouling potential reductions using a membrane hybrid system as a pre-treatment to seawater reverse osmosis. Appl Biochem Biotechnol 167(6):1716–1727
65. Jiang Y, Liang P, Liu P, Bian Y, Miao B, Sun X et al (2016) Enhancing signal output and avoiding BOD/toxicity combined shock interference by operating a microbial fuel cell sensor with an optimized background concentration of organic matter. Int J Mol Sci 17(9):1392
66. Jiang Y, Liang P, Liu P, Yan X, Bian Y, Huang X (2017) A cathode-shared microbial fuel cell sensor array for water alert system. Int J Hydrog Energy 42(7):4342–4348
67. Jiang Y, Yang X, Liang P, Liu P, Huang X (2018) Microbial fuel cell sensors for water quality early warning systems: fundamentals, signal resolution, optimization and future challenges. Renew Sustain Energy Rev 81:292–305

68. Kang CS, Eaktasang N, Kwon D-Y, Kim HS (2014) Enhanced current production by Desulfovibrio desulfuricans biofilm in a mediator-less microbial fuel cell. Biores Technol 165:27–30
69. Karube I, Matsunaga T, Mitsuda S, Suzuki S (1977) Microbial electrode BOD sensors. Biotechnol Bioeng 19(10):1535–1547
70. Kaur A, Kim JR, Michie I, Dinsdale RM, Guwy AJ, Premier GC et al (2013) Microbial fuel cell type biosensor for specific volatile fatty acids using acclimated bacterial communities. Biosens Bioelectron 47:50–55
71. Khatoon A, Mohd Setapar SH, Umar K, Parveen T, Mohamad Ibrahim MN, Rafatullah M (2020) Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. Catalysts 10(8):819
72. Kim BH, Chang IS, Gil GC, Park HS, Kim HJ (2003) Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. Biotech Lett 25(7):541–545
73. Kim JR, Cheng S, Oh S-E, Logan BE (2007) Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells. Environ Sci Technol 41(3):1004–1009
74. Kim M, Hyun MS, Gadd GM, Kim HJ (2007) A novel biomonitoring system using microbial fuel cells. J Environ Monit 9(12):1323–1328
75. Kim M, Lim JW, Kim HJ, Lee SK, Lee SJ, Kim T (2015) Chemostat-like microfluidic platform for highly sensitive detection of heavy metal ions using microbial biosensors. Biosens Bioelectron 65:257–264
76. Kim T, Han J-I (2013) Fast detection and quantification of Escherichia coli using the base principle of the microbial fuel cell. J Environ Manag 130:267–275
77. Kooij DVD (1992) Assimilable organic carbon as an indicator of bacterial regrowth. J-Am Water Works Assoc 84(2):57–65
78. Kumar AK, Reddy MV, Chandrasekhar K, Srikanth S, Mohan SV (2012) Endocrine disruptive estrogens role in electron transfer: bio-electrochemical remediation with microbial mediated electrogenesis. Biores Technol 104:547–556
79. Kumar R, Kumar A (2005) Water analysis| biochemical oxygen demand
80. Kumar R, Singh L, Zularisam A (2016) Exoelectrogens: recent advances in molecular drivers involved in extracellular electron transfer and strategies used to improve it for microbial fuel cell applications. Renew Sustain Energy Rev 56:1322–1336
81. Kumar SS, Malyan SK, Basu S, Bishnoi NR (2017) Syntrophic association and performance of Clostridium, Desulfovibrio, Aeromonas and Tetrathiobacter as anodic biocatalysts for bioelectricity generation in dual chamber microbial fuel cell. Environ Sci Pollut Res 24(19):16019–16030
82. Kumlanghan A, Liu J, Thavarungkul P, Kanatharana P, Mattiasson B (2007) Microbial fuel cell-based biosensor for fast analysis of biodegradable organic matter. Biosens Bioelectron 22(12):2939–2944
83. Le C, Zha Y, Li Y, Sun D, Lu H, Yin B (2010) Eutrophication of lake waters in China: cost, causes, and control. Environ Manag 45(4):662–668
84. Lee SH, Lee K-S, Sorcar S, Razzaq A, Grimes CA, In S-I (2018) Wastewater treatment and electricity generation from a sunlight-powered single chamber microbial fuel cell. J Photochem Photobiol A 358:432–440
85. Lei Y, Chen W, Mulchandani A (2006) Microbial biosensors. Anal Chim Acta 568(1–2):200–210
86. Li T, Wang X, Zhou Q, Liao C, Zhou L, Wan L et al (2018) Swift acid rain sensing by synergistic rhizospheric bioelectrochemical responses. ACS Sens 3(7):1424–1430
87. Li Y, Marshall A, Gostomski PA (2014) Gaseous pollutant treatment and electricity generation in microbial fuel cells (MFCs) utilising redox mediators. Rev Environ Sci Bio/Technol 13(1):35–51
88. Lincy MA, Kumar BA, Vasantha V, Varalakshmi P (2015) Microbial fuel cells: a promising alternative energy source. Oppor Challenges, 61
89. Liu B, Lei Y, Li B (2014) A batch-mode cube microbial fuel cell based "shock" biosensor for wastewater quality monitoring. Biosens Bioelectron 62:308–314

90. Liu H, Cheng S, Logan BE (2005) Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. Environ Sci Technol 39(2):658–662
91. Liu J, Mattiasson B (2002) Microbial BOD sensors for wastewater analysis. Water Res 36(15):3786–3802
92. Liu Z, Du Z, Lian J, Zhu X, Li S, Li H (2007) Improving energy accumulation of microbial fuel cells by metabolism regulation using Rhodoferax ferrireducens as biocatalyst. Lett Appl Microbiol 44(4):393–398
93. Liu Z, Liu J, Zhang S, Xing X-H, Su Z (2011) Microbial fuel cell based biosensor for in situ monitoring of anaerobic digestion process. Biores Technol 102(22):10221–10229
94. Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S et al (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40(17):5181–5192
95. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337(6095):686–690
96. Logan BE, Regan JM (2006) Electricity-producing bacterial communities in microbial fuel cells. Trends Microbiol 14(12):512–518
97. Lovley DR (2006) Bug juice: harvesting electricity with microorganisms. Nat Rev Microbiol 4(7):497–508
98. Lovley DR (2006) Microbial fuel cells: novel microbial physiologies and engineering approaches. Curr Opin Biotechnol 17(3):327–332
99. Magno M, Boyle D, Brunelli D, Popovici E, Benini L (2013) Ensuring survivability of resource-intensive sensor networks through ultra-low power overlays. IEEE Trans Industr Inf 10(2):946–956
100. Malvankar NS, Lovley DR (2012) Microbial nanowires: a new paradigm for biological electron transfer and bioelectronics. Chemsuschem 5(6):1039–1046
101. Mao L, Verwoerd WS (2013) Selection of organisms for systems biology study of microbial electricity generation: a review. Int J Energy Environ Eng 4(1):1–18
102. Markfort CD, Hondzo M (2009) Dissolved oxygen measurements in aquatic environments: the effects of changing temperature and pressure on three sensor technologies. J Environ Qual 38(4):1766–1774
103. Melhuish C, Ieropoulos I, Greenman J, Horsfield I (2006) Energetically autonomous robots: food for thought. Auton Robot 21(3):187–198
104. Miller LG, Oremland RS (2008) Electricity generation by anaerobic bacteria and anoxic sediments from hypersaline soda lakes. Extremophiles 12(6):837–848
105. Modestra JA, Mohan SV (2014) Bio-electrocatalyzed electron efflux in Gram positive and gram negative bacteria: an insight into disparity in electron transfer kinetics. RSC Adv 4(64):34045–34055
106. Modin O, Aulenta F (2017) Three promising applications of microbial electrochemistry for the water sector. Environ Sci: Water Res Technol 3(3):391–402
107. Modin O, Wilén B-M (2012) A novel bioelectrochemical BOD sensor operating with voltage input. Water Res 46(18):6113–6120
108. Mohan SV, Velvizhi G, Krishna KV, Babu ML (2014) Microbial catalyzed electrochemical systems: a bio-factory with multi-facet applications. Biores Technol 165:355–364
109. Mohan SV, Velvizhi G, Modestra JA, Srikanth S (2014) Microbial fuel cell: critical factors regulating bio-catalyzed electrochemical process and recent advancements. Renew Sustain Energy Rev 40:779–797
110. Mook WT, Aroua MKT, Chakrabarti MH, Noor IM, Irfan MF, Low CTJ (2013) A review on the effect of bio-electrodes on denitrification and organic matter removal processes in bio-electrochemical systems. J Ind Eng Chem 19(1):1–13
111. Mulchandani A (2011) Microbial biosensors for organophosphate pesticides. Appl Biochem Biotechnol 165(2):687–699
112. Naresh V, Lee N (2021) A review on biosensors and recent development of nanostructured materials-enabled biosensors. Sensors 21(4):1109
113. Nawaz A, Hafeez A, Abbas SZ, Haq IU, Mukhtar H, Rafatullah M (2020) A state of the art review on electron transfer mechanisms, characteristics, applications and recent advancements in microbial fuel cells technology. Green Chem Lett Rev 13(4):101–117

114. Niazi JH, Kim BC, Ahn J-M, Gu MB (2008) A novel bioluminescent bacterial biosensor using the highly specific oxidative stress-inducible pgi gene. Biosens Bioelectron 24(4):670–675
115. Oh S, Min B, Logan BE (2004) Cathode performance as a factor in electricity generation in microbial fuel cells. Environ Sci Technol 38(18):4900–4904
116. Pandit S, Chandrasekhar K, Kakarla R, Kadier A, Jeevitha V (2017) Basic principles of microbial fuel cell: technical challenges and economic feasibility. In: Microbial applications, vol 1. Springer, pp 165–188
117. Pandit S, Khilari S, Roy S, Ghangrekar M, Pradhan D, Das D (2015) Reduction of start-up time through bioaugmentation process in microbial fuel cells using an isolate from dark fermentative spent media fed anode. Water Sci Technol 72(1):106–115
118. Pandit S, Khilari S, Roy S, Pradhan D, Das D (2014) Improvement of power generation using Shewanella putrefaciens mediated bioanode in a single chambered microbial fuel cell: effect of different anodic operating conditions. Biores Technol 166:451–457
119. Pant D, Van Bogaert G, Diels L, Vanbroekhoven K (2010) A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Biores Technol 101(6):1533–1543
120. Park D, Zeikus J (2000) Electricity generation in microbial fuel cells using neutral red as an electronophore. J Appl Environ Microb 66:1292–1297
121. Park HS, Kim BH, Kim HS, Kim HJ, Kim GT, Kim M et al (2001) A novel electrochemically active and Fe (III)-reducing bacterium phylogenetically related to Clostridium butyricum isolated from a microbial fuel cell. Anaerobe 7(6):297–306
122. Parkhey P, Mohan SV (2019) Biosensing applications of microbial fuel cell: Approach toward miniaturization. In: Microbial electrochemical technology. Elsevier, pp 977–997
123. Pasternak G, Greenman J, Ieropoulos I (2017) Self-powered, autonomous biological oxygen demand biosensor for online water quality monitoring. Sens Actuat B Chem 244:815–822
124. Petrie B, Barden R, Kasprzyk-Hordern B (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res 72:3–27
125. Porcarelli D, Brunelli D, Benini L (2012) Characterization of lithium-ion capacitors for low-power energy neutral wireless sensor networks. 2012 ninth international conference on networked sensing (INSS). IEEE, pp 1–4
126. Potter M (1910) On the difference of potential due to the vital activity of microorganisms. In: Proceedings of the University of Durham philosophical society, pp 245–249
127. Prévoteau A, Clauwaert P, Kerckhof F-M, Rabaey K (2019) Oxygen-reducing microbial cathodes monitoring toxic shocks in tap water. Biosens Bioelectron 132:115–121
128. Quek SB, Cheng L, Cord-Ruwisch R (2015) Microbial fuel cell biosensor for rapid assessment of assimilable organic carbon under marine conditions. Water Res 77:64–71
129. Realtech (2021) Biochemical oxygen demand (BOD). https://realtechwater.com/parameters/biochemical-oxygen-demand/. Accessed 17 June 2021
130. Rimboud M, Pocaznoi D, Erable B, Bergel A (2014) Electroanalysis of microbial anodes for bioelectrochemical systems: basics, progress and perspectives. Phys Chem Chem Phys 16(31):16349–16366
131. Rosenbaum M, Aulenta F, Villano M, Angenent LT (2011) Cathodes as electron donors for microbial metabolism: which extracellular electron transfer mechanisms are involved? Biores Technol 102(1):324–333
132. Saha TC, Protity AT, Zohora FT, Shaha M, Ahmed I, Barua E et al (2019) Microbial fuel cell (MFC) application for generation of electricity from dumping rubbish and identification of potential electrogenic bacteria. Adv Ind Biotechnol 2(10)
133. Sai ASV (2009) Microbial fuel cells: principles and applications. Altenergymag. https://www.altenergymag.com/article/2009/12/microbial-fuel-cellsprinciples-and-applications/587
134. Schamphelaire LD, Bossche LVD, Dang HS, Höfte M, Boon N, Rabaey K et al (2008) Microbial fuel cells generating electricity from rhizodeposits of rice plants. Environ Sci Technol 42(8):3053–3058

135. Schneider G, Czeller M, Rostás V, Kovács T (2015) Microbial fuel cell-based diagnostic platform to reveal antibacterial effect of beta-lactam antibiotics. Enzyme Microb Technol 73:59–64
136. Schneider G, Kovács T, Rákhely G, Czeller M (2016) Biosensoric potential of microbial fuel cells. Appl Microbiol Biotechnol 100(16):7001–7009
137. Schwarzenbach RP, Egli T, Hofstetter TB, Von Gunten U, Wehrli B (2010) Global water pollution and human health. Annu Rev Environ Resour 35:109–136
138. Shen H-B, Yong X-Y, Chen Y-L, Liao Z-H, Si R-W, Zhou J et al (2014) Enhanced bioelectricity generation by improving pyocyanin production and membrane permeability through sophorolipid addition in Pseudomonas aeruginosa-inoculated microbial fuel cells. Biores Technol 167:490–494
139. Shen Q, Zhou Q, Shang J, Shao S, Zhang L, Fan C (2014) Beyond hypoxia: occurrence and characteristics of black blooms due to the decomposition of the submerged plant Potamogeton crispus in a shallow lake. J Environ Sci 26(2):281–288
140. Shen Y, Wang M, Chang IS, Ng HY (2013) Effect of shear rate on the response of microbial fuel cell toxicity sensor to Cu(II). Biores Technol 136:707–710
141. Shen YJ, Lefebvre O, Tan Z, Ng HY (2012) Microbial fuel-cell-based toxicity sensor for fast monitoring of acidic toxicity. Water Sci Technol 65(7):1223–1228
142. Shin HJ (2010) Development of highly-sensitive microbial biosensors by mutation of the nahR regulatory gene. J Biotechnol 150(2):246–250
143. Si R-W, Zhai D-D, Liao Z-H, Gao L, Yong Y-C (2015) A whole-cell electrochemical biosensing system based on bacterial inward electron flow for fumarate quantification. Biosens Bioelectron 68:34–40
144. Song N, Jiang H-L (2018) Effects of initial sediment properties on start-up times for sediment microbial fuel cells. Int J Hydrog Energy 43(21):10082–10093
145. Song N, Yan Z, Xu H, Yao Z, Wang C, Chen M et al (2019) Development of a sediment microbial fuel cell-based biosensor for simultaneous online monitoring of dissolved oxygen concentrations along various depths in lake water. Sci Total Environ 673:272–280
146. Stein NE, Hamelers HM, van Straten G, Keesman KJ (2012) On-line detection of toxic components using a microbial fuel cell-based biosensor. J Process Control 22(9):1755–1761
147. Stein NE, Hamelers HV, Buisman CN (2010) Stabilizing the baseline current of a microbial fuel cell-based biosensor through overpotential control under non-toxic conditions. Bioelectrochemistry 78(1):87–91
148. Sun J-Z, Peter Kingori G, Si R-W, Zhai D-D, Liao Z-H, Sun D-Z et al (2015) Microbial fuel cell-based biosensors for environmental monitoring: a review. Water Sci Technol 71(6):801–809
149. Tan T, Li F, Neoh K, Lee Y (1992) Microbial membrane-modified dissolved oxygen probe for rapid biochemical oxygen demand measurement. Sens Actuat B Chem 8(2):167–172
150. Tardy GM, Lóránt B, Gyalai-Korpos M, Bakos V, Simpson D, Goryanin I (2021) Microbial fuel cell biosensor for the determination of biochemical oxygen demand of wastewater samples containing readily and slowly biodegradable organics. Biotech Lett 43(2):445–454
151. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ (2012) Heavy metal toxicity and the environment. Mol Clin Environ Toxicol, 133–164
152. Thurston C, Bennetto H, Delaney G, Mason J, Roller S, Stirling J (1985) Glucose metabolism in a microbial fuel cell. Stoichiometry of product formation in a thionine-mediated Proteus vulgaris fuel cell and its relation to coulombic yields. Microbiology, 131(6):1393–1401
153. Tran PHN, Luong TTT, Nguyen TTT, Nguyen HQ, Van Duong H, Kim BH (2015) Possibility of using a lithotrophic iron-oxidizing microbial fuel cell as a biosensor for detecting iron and manganese in water samples. Environ Sci Process Impacts 17(10):1806–1815
154. Vogrinc D, Vodovnik M, Marinšek-Logar R (2015) Microbial biosensors for environmental monitoring. Acta Agricult Slovenica 106(2):67–75
155. Von Canstein H, Ogawa J, Shimizu S, Lloyd JR (2008) Secretion of flavins by Shewanella species and their role in extracellular electron transfer. Appl Environ Microbiol 74(3):615–623

156. Wang G-H, Cheng C-Y, Liu M-H, Chen T-Y, Hsieh M-C, Chung Y-C (2016) Utility of Ochrobactrum anthropi YC152 in a microbial fuel cell as an early warning device for hexavalent chromium determination. Sensors 16(8):1272
157. Wang H, Ren ZJ (2013) A comprehensive review of microbial electrochemical systems as a platform technology. Biotechnol Adv 31(8):1796–1807
158. Wang X, Liu M, Wang X, Wu Z, Yang L, Xia S et al (2013) P-benzoquinone-mediated amperometric biosensor developed with Psychrobacter sp. for toxicity testing of heavy metals. Biosens Bioelectron 41:557–562
159. Wei T, Zhang C, Xu X, Hanna M, Zhang X, Wang Y et al (2013) Construction and evaluation of two biosensors based on yeast transcriptional response to genotoxic chemicals. Biosens Bioelectron 44:138–145
160. Wu L-C, Tsai T-H, Liu M-H, Kuo J-L, Chang Y-C, Chung Y-C (2017) A green microbial fuel cell-based biosensor for in situ chromium (VI) measurement in electroplating wastewater. Sensors 17(11):2461
161. Wu S, Deng H, Han C, Liu L, Zhong W (2018) A novel sediment microbial fuel cell based sensor for on-line and in situ monitoring copper shock in water. Electroanalysis 30(11):2668–2675
162. Wu W, Lesnik KL, Xu S, Wang L, Liu H (2014) Impact of tobramycin on the performance of microbial fuel cell. Microb Cell Fact 13(1):1–7
163. Xafenias N, Zhang Y, Banks CJ (2013) Enhanced performance of hexavalent chromium reducing cathodes in the presence of Shewanella oneidensis MR-1 and lactate. Environ Sci Technol 47(9):4512–4520
164. Xu D, Gu T (2014) Carbon source starvation triggered more aggressive corrosion against carbon steel by the Desulfovibrio vulgaris biofilm. Int Biodeter Biodegrad 91:74–81
165. Xu D, Li Y, Song F, Gu T (2013) Laboratory investigation of microbiologically influenced corrosion of C1018 carbon steel by nitrate reducing bacterium Bacillus licheniformis. Corros Sci 77:385–390
166. Xu X, Ying Y (2011) Microbial biosensors for environmental monitoring and food analysis. Food Rev Intl 27(3):300–329
167. Xu Z, Liu B, Dong Q, Lei Y, Li Y, Ren J et al (2015) Flat microliter membrane-based microbial fuel cell as "on-line sticker sensor" for self-supported in situ monitoring of wastewater shocks. Biores Technol 197:244–251
168. Yang G-X, Sun Y-M, Kong X-Y, Zhen F, Li Y, Li L-H et al (2013) Factors affecting the performance of a single-chamber microbial fuel cell-type biological oxygen demand sensor. Water Sci Technol 68(9):1914–1919
169. Yang H, Zhou M, Liu M, Yang W, Gu T (2015) Microbial fuel cells for biosensor applications. Biotech Lett 37(12):2357–2364
170. Yang M (2011) A current global view of environmental and occupational cancers. J Environ Sci Health C 29(3):223–249
171. Yang W, Wei X, Fraiwan A, Coogan CG, Lee H, Choi S (2016) Fast and sensitive water quality assessment: a μL-scale microbial fuel cell-based biosensor integrated with an air-bubble trap and electrochemical sensing functionality. Sens Actuat B Chem 226:191–195
172. Yang Z, Suzuki H, Sasaki S, Karube I (1996) Disposable sensor for biochemical oxygen demand. Appl Microbiol Biotechnol 46(1):10–14
173. Yong D, Liu C, Yu D, Dong S (2011) A sensitive, rapid and inexpensive way to assay pesticide toxicity based on electrochemical biosensor. Talanta 84(1):7–12
174. Yong Y-C, Zhong J-J (2009) A genetically engineered whole-cell pigment-based bacterial biosensing system for quantification of N-butyryl homoserine lactone quorum sensing signal. Biosens Bioelectron 25(1):41–47
175. Yu D, Bai L, Zhai J, Wang Y, Dong S (2017) Toxicity detection in water containing heavy metal ions with a self-powered microbial fuel cell-based biosensor. Talanta 168:210–216
176. Yaqoob AA, Ibrahim MNM, Yaakop AS, Ahmad A (2021) Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. Appl Nanosci 11(6):1949–1961

177. Zeng L, Li X, Shi Y, Qi Y, Huang D, Tadé M et al (2017) FePO4 based single chamber air-cathode microbial fuel cell for online monitoring levofloxacin. Biosens Bioelectron 91:367–373
178. Zhang C, Liang P, Jiang Y, Huang X (2015) Enhanced power generation of microbial fuel cell using manganese dioxide-coated anode in flow-through mode. J Power Sour 273:580–583
179. Zhang M, Yu Y, Yang Z, Shi X, Kong F (2012) The distribution of phytoplankton along trophic gradients and its mediation by available light in the pelagic zone of large eutrophic lakes. Can J Fish Aquat Sci 69(12):1935–1946
180. Zhang Y, Angelidaki I (2012) A simple and rapid method for monitoring dissolved oxygen in water with a submersible microbial fuel cell (SBMFC). Biosens Bioelectron 38(1):189–194
181. Zhao F, Harnisch F, Schröder U, Scholz F, Bogdanoff P, Herrmann I (2006) Challenges and constraints of using oxygen cathodes in microbial fuel cells. Environ Sci Technol 40(17):5193–5199
182. Zhao S, Liu P, Niu Y, Chen Z, Khan A, Zhang P et al (2018) A novel early warning system based on a sediment microbial fuel cell for in situ and real time hexavalent chromium detection in industrial wastewater. Sensors 18(2):642
183. Zhou T, Han H, Liu P, Xiong J, Tian F, Li X (2017) Microbial fuels cell-based biosensor for toxicity detection: a review. Sensors 17(10):2230

Microbial Fuel Cells—A Sustainable Approach to Clean Energy and Wastewater Remediation

Nishat Khan, Abdul Hakeem Anwer, and Mohammad Zain Khan

Abstract The chapter deals with the brief introduction to water and energy crisis. Further, it presents a detailed introduction of microbial fuel cell (MFC) technology discussing its various components, types and different substrates treatable in MFC with various terminal electron acceptors utilised in it along with critical literature survey of last 5 years. As the fossil fuels stand on the edge of extinction, studies for new and potential renewable resources have become a focus of scientific research. The need to look for alternatives brought the scientific community to the domain of waste harvesting to generate potential renewable resources that can take the reign of energy generation from fossil fuels to lead the human civilisation to new highs in near future. MFC technology has recently garnered considerable attention due to its unique nature to create a symbiotic relationship between the wastewater and electric output. It works on the principle of redox reaction where the wastewater present in the anodic compartment generates electrons to flow through the circuit and produce current. An MFC system can treat a wide variety of waste streams ranging from simple substrate like glucose/acetate to more complex substrates like domestic/industrial wastewater. Several novel designs of MFC have been suggested over the years with the same basic idea of anaerobic anode and aerobic cathode. MFC presents a promising approach for waste treatment contrary to the conventional technologies with zero energy input, low sludge production, compact designing with no movable parts for easy handling and efficient performance.

Keywords Biotreatment · Electron transfer · Microbial fuel cell · Power density · Wastewater

N. Khan (✉) · A. H. Anwer · M. Z. Khan
Environmental Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh 202002, UP, India
e-mail: nishatk57@gmail.com

M. Z. Khan
e-mail: dr_mzain.ch@amu.ac.in

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_18

1 The Major Concerns

Water and energy are the two critical and extensively expanding demands of the twenty-first century's sustainable society. Scarcity or lack of freshwater, according to World Health Organisation (WHO), affects more than 40% of the world's population [192]. Water finds application in every aspect of life ranging from agriculture to domestic and industrial processes. These water utilising sources release effluents with undesirable pH, colour, odour, temperature and chemicals, termed as wastewater. This wastewater when mixed with fresh water and utilised for different purposes causes various health hazards. Clean and freshwater is a basic need of all living organisms. However, the toxicants such as dyes, pesticides, drugs and metal ions when present in the potable water induce severe environmental and health issues. They have high bioaccumulation potential, which is another serious and important concern. Figure 1 presents some facts about water—its distribution and pollution (WHO and UN-Water sites) [148, 159]. Recently, wastewater released from various sources like domestic and factory effluent has gained attention as a potential resource of renewable energy to harvest electric energy and offset the wastewater treatment cost, which is otherwise high for conventional treatment technologies.

Further, the energy demand is continuously increasing around the world and most of this demand is fulfilled through fossil fuels. The development of all the economies around the world has been supported by these fuels for centuries by expanded industrialisation. However, with the limited availability, threatened depletion and the drastic consequence of fossil fuels on the environment (greenhouse gases (GHGs) emission), focus has shifted to sustainable and renewable sources of energy, a much-needed alternative to fulfil the energy demand efficiently and cleanly. Nonetheless, data released by International Energy Agency (IEA) in 2017 [62] reflected that the renewable resources only account for around 23% of the total energy produced (Fig. 2). Biofuels, in the recent years, have drawn worldwide attention in this context. In near future, bioelectricity can serve as a potential source of fuel to serve the purpose of energy requirement on a larger scale. It is a renewable source of energy with potential to become a replacement of fossil fuels for power production in future [96]. Thus, it can serve as GHG neutral alternative to the conventional energy sources (e.g., fossil fuels), which release heavy amounts of GHGs into the atmosphere thus intensifying global warming [100, 157]. Industrial and agricultural wastewater has high organic content that can be utilised to derive energy. Data released by IEA in 2017 reflected, however, that these resources (biomass and waste) only account for around 2% of the total energy produced globally (Fig. 2). Also, country-wise energy generation data suggest that Asian countries like China and India have high energy demand, which is expected to grow in the near future as per IEA energy outlook 2019 [63] (Fig. 3).

India is among the top 10 countries in the world facing the worst water crisis as nearly 54% population of India lives under water stress. With heavy consumption, 21 cities (including Delhi, Chennai) are estimated to run out of groundwater in very near future. By 2030, early 40% of Indian population may be affected with nearly no access to fresh drinking water as water demand will rise from 650 in 2008 to

Fig. 1 Facts about water—its distributions and pollution

1498 billion cubic meters by 2030. On the other hand, with increasing development in both urban and rural sectors of the country, the energy demand is continuously increasing with the overall energy consumption of 1561 TWh in 2018 as compared to 1317 TWh in 2015. By 2040, the Indian share of global energy demand is estimated to increase by 2 times and with coal being the major source, the CO_2 emission will simultaneously be roughly doubled worsening its effect of environment. India is in urgent need to counter these growing concerns in an environmentally friendly way to pave way for a better future.

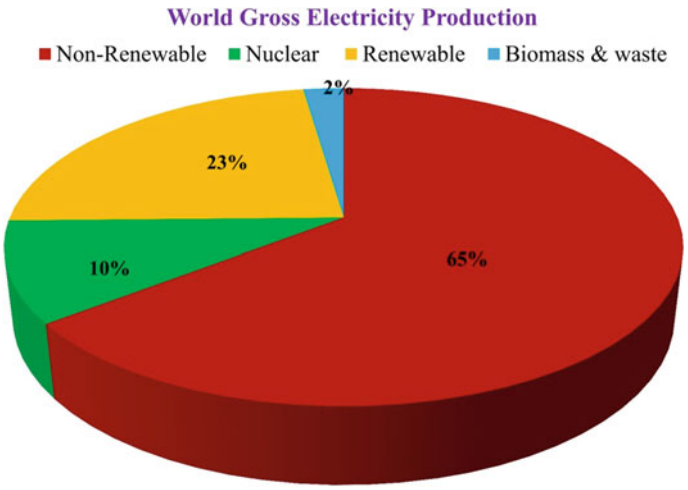

Fig. 2 Different sources of electricity production

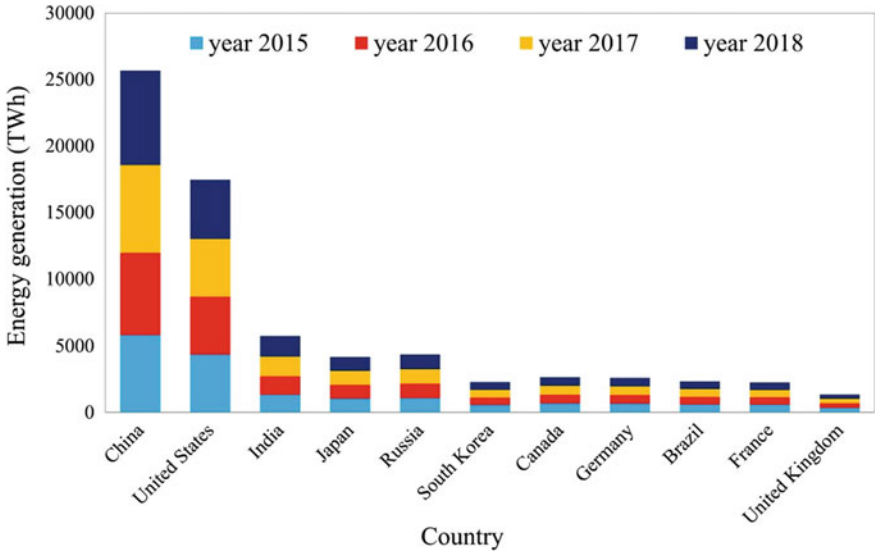

Fig. 3 Country-wise electricity generation in TWh. *Source* BP Statistics

2 Renewable Sources of Energy

The world has seen different eras of energy from charcoal to coal to oil era of twentieth century (Fig. 4). Owing to their threatened depletion and environmental effects, these non-renewable resources are being replaced with more renewable ones.

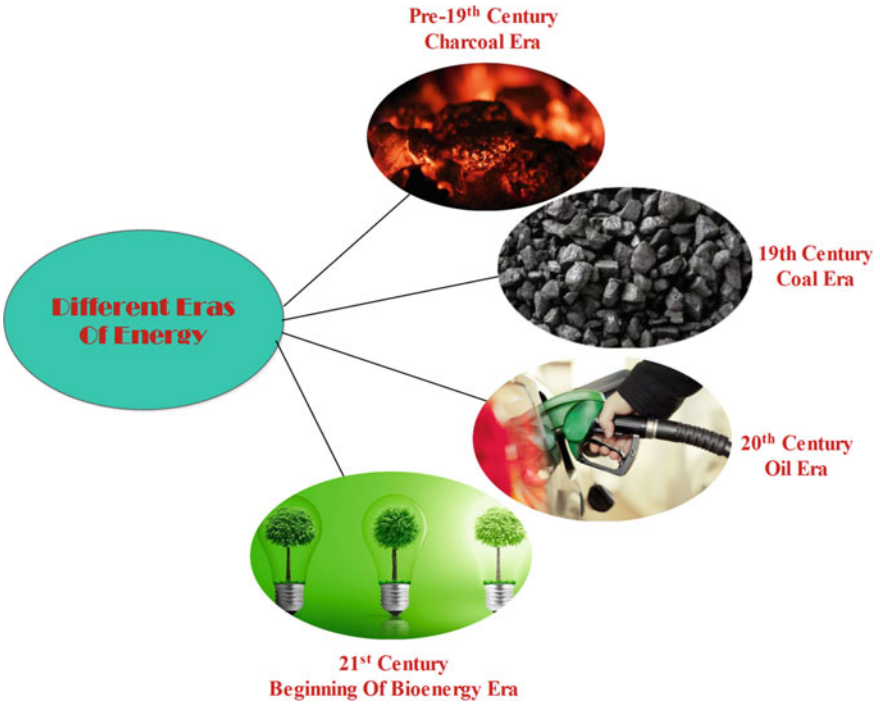

Fig. 4 Different eras of energy

Resources that can be repeatedly replenished in nature and do not run out with time are known as renewable resources, and energy produced from these resources is known as renewable energy or clean energy. Solar, wind, tidal, hydro and geothermal energies have been successfully employed to harvest renewable energy around the world. Figure 5 presents the flowchart of the various techniques available for generating renewable energy. Recently, bioenergy has garnered significant attention as a potential renewable energy source marking twenty-first century as the beginning of era of bioenergy. Bioenergy is the energy derived from biomass, which ranges from food waste and plants to wastewater [125].

In the recent years, as the direct derivation of renewable energy from the waste has become a potential option, bioelectrochemical systems have played a significant role in extraction of usable energy from waste.

Different bioelectrochemical systems have been developed over the years with microbial fuel cell (MFC) being the most explored technology. Figure 6 presents the number of papers published on different bioenergy techniques (MFC, MDC, MEC, and BES) while Fig. 7 shows the papers published on MFC between 2015 and January 2020 according to Web of Science data search.

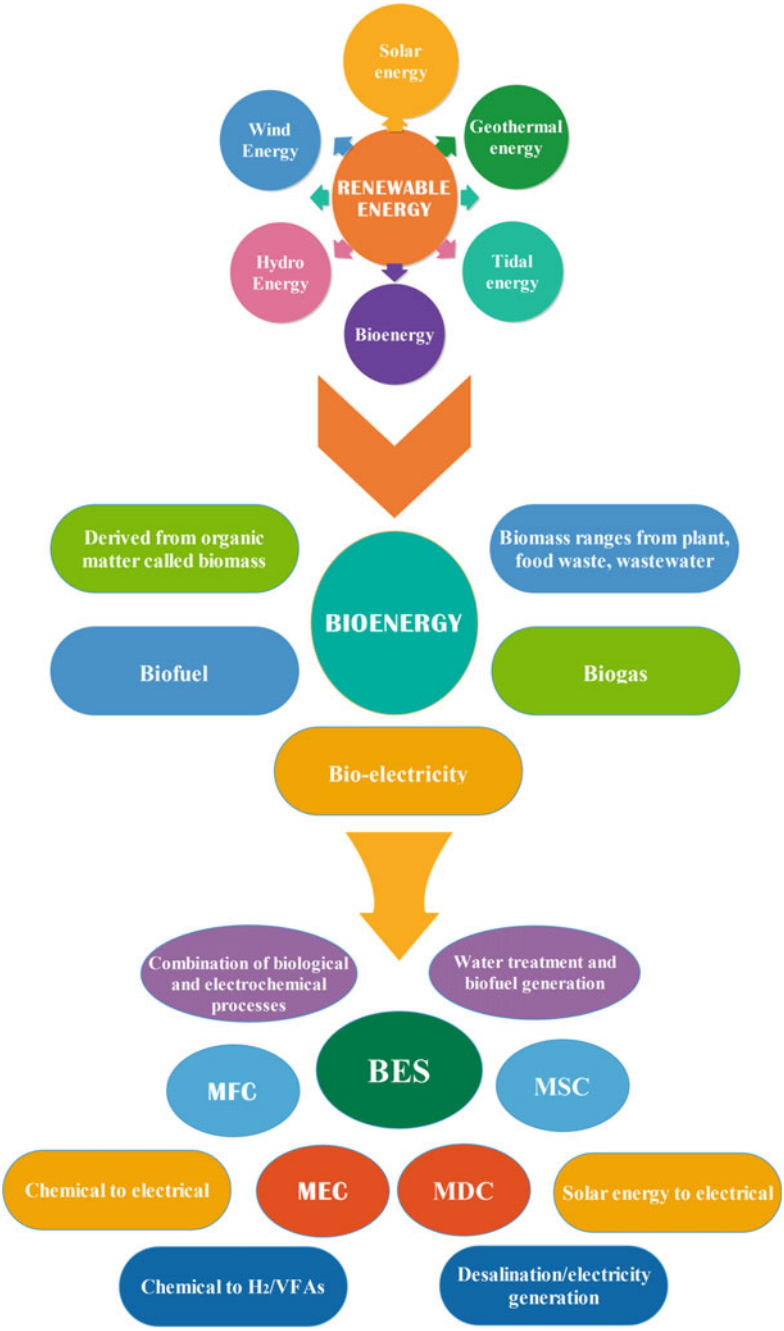

Fig. 5 Flow diagram showing different sources of renewable energy with special reference to bioenergy

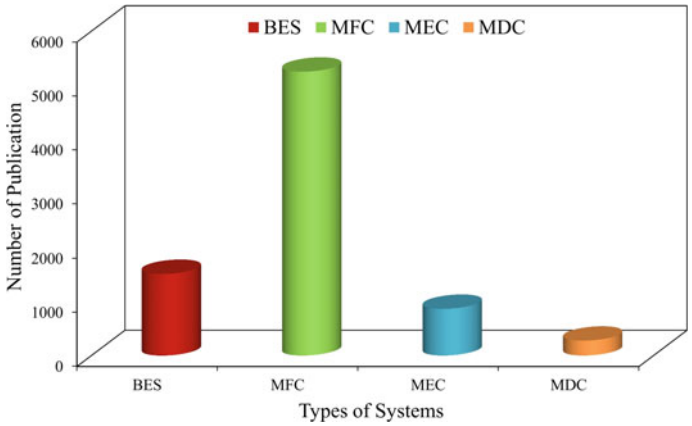

Fig. 6 Quantitative analysis of number of papers published for various types of systems over last 5 years. *Source* Web of Science

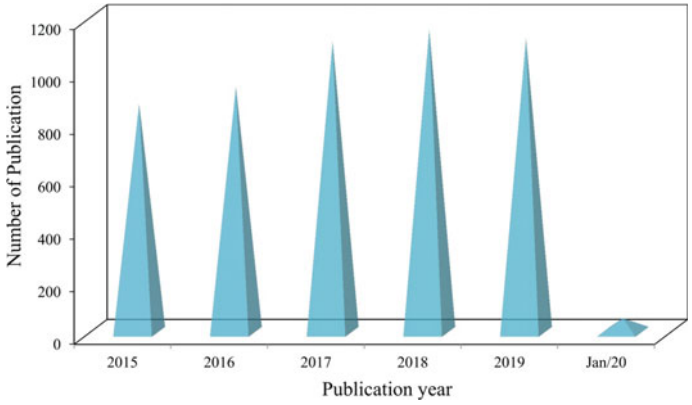

Fig. 7 Number of papers published over the last 5 years on microbial fuel cell. *Source* Web of Science, January 2020

3 Microbial Fuel Cell Technology

The need and interest in finding the sustainable alternatives to the non-renewable sources of energy that are cost-effective and performance efficient have brought the focus of the scientists across the world to MFC technology (Fig. 8). MFC is a technology capable of harvesting energy from organic and inorganic chemical wastes in the form of electricity. The technology has garnered significant attention because of its capability of harvesting energy from waste with almost zero energy input [79]. MFC can be defined as the technology that utilises active microbial population to catalyse the oxidation of organic and inorganic waste to harvest energy in the form

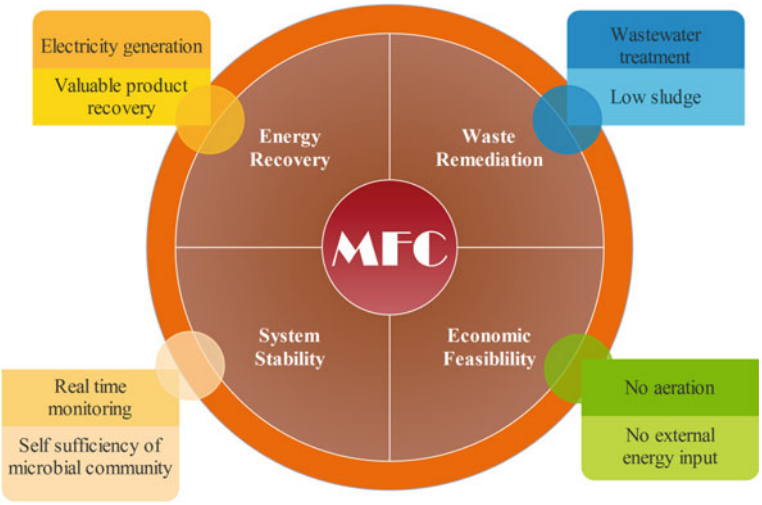

Fig. 8 Significance of microbial fuel cell

of bioelectricity. It acts as a connecting link between microbial metabolism and electrochemistry of the system [79]. The first idea of harvesting electric energy with the aid of microorganisms' dates back to the early twentieth century when Potter and coworkers in 1911 suggested that living cultures like *E. coli* and *Sacchromyces* can assist in the production of electricity. However, the work did not gain much attention until the 1931 work by Cohen, who connected MFCs in series producing voltage larger than 35 V [157]. Further, NASA in 1960s researched the applications of MFCs in space missions. Later, in 1980s, Allen and Bennetto discovered that the performance of MFC can be greatly improved by using mediators to support electron conduction from microbes to the electrodes. However, the instability and toxicity of the mediators offered obstructions in their practical application. A major breakthrough came when Kim et al. in 1999 [63] showed that the electricity conduction does not require mediators and some microbial communities can transfer electrons to the electrodes directly using microbial metabolites. Bruce Logan and team are considered to be the first to develop a laboratory-scale MFC [48, 124]. The basic principle of MFC is based on the redox reaction taking place within the system where the oxidation taking place at the anode generates electrons and protons lowering the redox potential at the anode. The electrons produced travel through the external circuit while the protons migrate across the membrane to the cathode where they are accepted by the terminal electron acceptor (TEA) at higher redox potential. The flow of electron across the circuit as a result of developed potential gradient generates electrical energy [56]. The oxidation product formed in the anodic chamber during the process is carbon dioxide and as most of the carbon dioxide in the renewable biomass is originally coming from the fixation of atmospheric carbon dioxide through photosynthesis, no net carbon emission is made into the environment by MFC [39]. However, the electricity generation can be dramatically inhibited if oxygen contaminates the anodic chamber

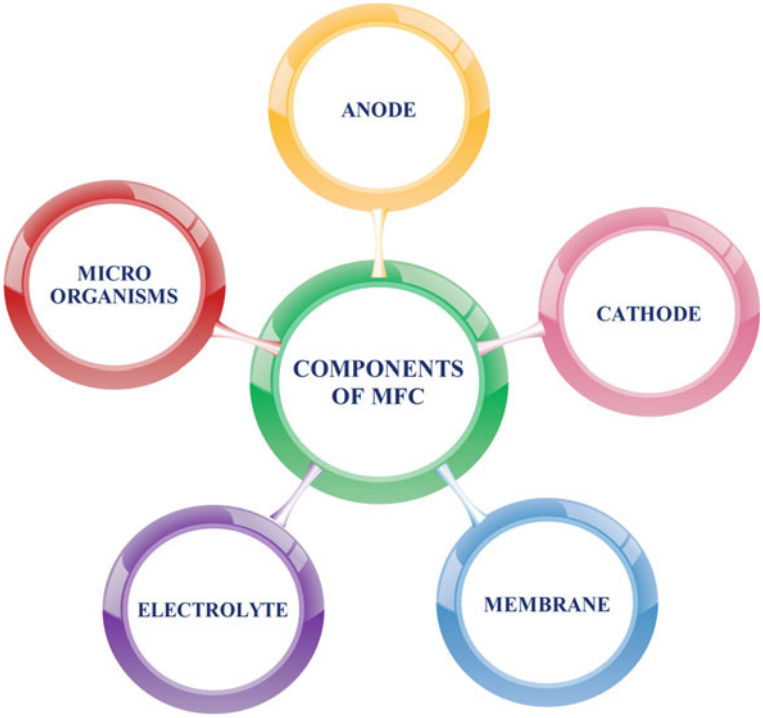

Fig. 9 Components of MFC

affecting the performance of anaerobic microbes adversely, which can be avoided by maintaining completely anaerobic conditions in the anodic chamber [39, 120].

MFC is a systematic arrangement of various components that collectively work to run the system. The five main building blocks of MFC are presented in Fig. 9.

Anode

Anodic chamber is one of the core elements of MFC as all the pre-requisites for degrading the biomass is provided in this chamber like the substrate to be degraded, microorganisms, mediators, and electron accepting anode. Bio-anode is sometimes described as the defining part of the MFC and can often act as the limiting factor for the MFC performance [124]. The choice of anode material also affects the performance as the shape, structure and material of the anode can affect the factors like bacterial adhesion, electron transfer and substrate metabolism. Some crucial properties to be considered while choosing a potential anode are its conductivity, biocompatibility, chemical stability in the electrolyte and specific surface area. Carbonaceous materials like graphite rods and plates, carbon paper, carbon cloth, carbon mesh, carbon felt, carbon fibre brush, reticulated vitreous carbon are the most widely used electrode material because of their high stability, conductive and biocompatible nature with simultaneous high surface area [96].

Considering that anode has significant impact on the overall performance of MFC, several strategies have been employed over the years to modify the anode in a bid to improve the MFC power output. Strategies have been adopted to increase the biocompatibility and surface area of the anode through acid, ammonia and heat treatment. In 2007, Cheng and Logan improved the output power density (PD) of the carbon cloth utilising MFC by treatment with ammonia and enhancing the surface charge on the electrode [25]. Cai et al. [14] compared the performance of MFC utilising a plain, nitric acid-treated and heat-treated carbon cloth electrodes and observed that the heat-treated electrode outperformed the other two and the improvement in the power output was mainly attributed to the improved biocompatibility of the electrode [14]. Furthermore, other researchers employed the techniques of nanoengineering to modify anodes where, conducting polymers like polyaniline (PANI) and polypyrrole (PPy) and carbon-based nanomaterials are the prime area of focus. Lai et al. [81] performed the electropolymerisation of PANI on carbon cloth and observed enhanced electrochemical activity, increased roughness for better biofilm formation with a relatively sustainable and reproducible MFC power output [81]. Qiao et al. [117] successfully reported carbon nanotube (CNT)/PANI as a feasible electrode material [117]. Zou et al. [196] harvested electric energy from *E. coli* catalysed MFC utilising a CNT/PPy coated carbon paper electrode [196]. Zhang et al. [190] studied the performance of graphene-modified stainless steel mesh anode and observed 18 folds improvement in the performance as compared to plain stainless-steel mesh as a result of enhanced electron transfer efficiency owing to improved surface area and better bacterial adhesion [190]. More recently, Tang et al. [142] used anthraquinone-2 sulfonate immobilised conductive polypyrrole hydrogel to significantly enhance the power output and reduce the charge transfer resistance of electrodes [142].

Another relevant factor that must be kept in mind while selecting anode is its potential. It defines the MFC power generation by monitoring the bacterial community and substrate interaction. Electrochemical analysis suggests that to achieve highest electric output the anode should have a low while cathode should have high electrode potential. However, the bioelectrochemical studies suggest a better bacterial colonisation at more positive anodic potential. Thus, to maximise the MFC current and power output performance, a careful tuning of anode potential is crucial [124]. Pinto et al. [115] investigated the effect of anodic potential on biofilm formation and electroactivity of *Shewanella oneidensis* and observed that the negative potential of −0.3 V favoured the mediated electron transfer while the positive anodic potential of +0.3 V favours faster colonisation of the microbial population on the electrode [115].

Cathode

Cathode is responsible for transferring the electrons travelling from anodic to the cathodic chamber and subsequently to TEA. Oxygen is generally the most frequently used electron acceptor owing to its ease of accessibility, free cost, high oxidation potential with no possibility of production of poisonous chemical waste as the end product of oxygen reduction is water [147]. However, the sluggish reduction kinetics of oxygen makes it a restricting agent in MFCs owing to the large potential loss and

thus acts as a major bottleneck in the electrical applications of MFC. Potassium ferricyanide is another popular electron acceptor that shows significant improvement in the power output, which could be due to the improved mass transfer rate and reduced activation energy required for the cathodic reaction [114]. However, ferricyanide shows a major drawback of regeneration and needs refilling frequently [120]. Several other TEAs have been explored over the years. Dai et al. [31] explored the potential of sodium bromate as an electron acceptor and observed the catholyte pH to decrease with the increasing concentration of sodium bromate thereby improving the performance of MFC [31]. Kumar et al. [80] compared the performance of four different electron acceptors namely buffered ferric chloride, potassium hexacyanoferrate, potassium dichromate and phosphate buffer solution (PBS) and observed the highest bioelectric performance in case of ferric chloride with the output PD of 308.7 mW/m^2. It was also reported that the internal resistance of MFC with different catholytes decreased in the order of potassium dichromate > hexacyanoferrate > ferric chloride > PBS [80]. Oon et al. [111] compared the performance of different monoazo (New Coccine and Acid Orange 7) and diazo dyes (Reactive Red 120 and Reactive green 19) as potential electron acceptors and reported that the decolorisation rate was nearly 50% higher for monoazo dyes as compared to the diazo dyes and the decolorisation and power output followed the trend; New Coccine > Acid Orange 7 > Reactive Red 120 > Reactive green 19 suggesting that the structure of the dye affected the decolorisation rate and power output [111]. Among the variety of TEAs explored so far, the free and easy access to oxygen still makes it the most opted electron acceptor. In a bid to enhance the oxygen reduction reaction rate (ORR) and lower the activation energy, the use of appropriate catalyst becomes important. Platinum (Pt) is the most widely known and explored catalyst showing a higher ORR calatalytic activity [12, 43, 116]. However, the use of Pt catalyst tremendously increases the operating cost of MFC and presents a major drawback of substrate poisoning in certain solutions [59]. Recently a variety of materials have been explored as ORR catalysts. For MFC, an ideal ORR catalyst should be cost-effective (keeping MFCs economically feasible), durable, synthesisable on large scale, and showing elevated catalytic activities. The catalysts used in cathode can be broadly divided into two categories, namely, (i) abiotic catalysts and (ii) biotic or biocatalysts [180]. The abiotic catalysts can be further subdivided into carbon-based catalysts like carbon black (CB), activated carbon (AC), carbon nanofibres (mainly CNTs) and graphene; metal-based catalysts; metal-carbon hybrids; and metal-nitrogen-carbon hybrid.

CB has been widely used in MFC as a metal catalyst supporting material. CNTs have garnered significant attention because of its high surface area and electric conductivity. The CNT-based catalysts can be easily tuned by doping with other components to achieve desired properties [173]. Also, CNT-based catalysts have been reported to have better durability than Pt-based catalysts [180]. Graphene has also recently received a lot of attention because of its higher stability and conductivity [136]. Graphene is comparable to CNTs in terms of cost-effectiveness but still lags behind the AC [180]. Macheri et al. [102] studied the performance of zirconium oxide (ZrO_2)/CB cathode with different concentrations of ZrO_2 (0, 25, 50, 75 and 100%) and observed that the ORR catalytic activity of ZrO_2/CB cathode with 25 wt%

of ZrO_2 was better compared to the other cathodes with the maximum PD of 600 mW/m^2 in a single chambered MFC. Also, the study reported that the assembling cost of ZrO_2/CB catalyst was 15 times less than Pt/CB cathode thereby decreasing the operating cost of the MFC [102]. Das et al. [34] synthesised a metal-based ORR catalyst using surface modified ferrite with Co and Zn in 1:1 ratio and observed the results to be comparable to 10% Pt/C-based catalyst with the maximum PD of 176.42 mW/m^2, a high Coulombic efficiency (CE) of 43.3% and maximum COD removal efficiency of 87% [34]. A novel Fe/N doped graphene/CNT composite was synthesised by Wang et al. [150]. The study revealed the synthesised nanocomposite to possess improved electrogenic and high electrocatalytic activity in the neutral PBS medium for ORR. They also reported that the synthesised composite displays higher MFC power output of 1210 mW/m^2 as compared to the Pt/C catalyst (1080 mW/m^2). The results of the work performed by Wang et al. concluded that the Fe-N/G with CNT possesses enhanced ORR capacity compared to Pt/C, which could be due to the high pyridine doped CNT or increased ORR active sites [150]. In another recently published study, a low-cost AC supported F-N-C catalyst was synthesised and used as cathode, which improved the PD of MFC by around 33% as compared to the plain AC. The synthesised composite also displayed good stability with no surface morphology change during the experiment [171]. Further, in the research carried out by Majidi et al. [98], an α-MnO_2 nanowire supported carbon vulcan was employed as ORR cathode catalyst. The study reported that the α-MnO_2/carbon vulcan can serve as an effective and economically feasible Pt free MFC catalyst on large scale because of its increased redox activity owing to its surface structure and increased surface area [98].

Microorganisms can also play the role of active ORR catalyst by acting as electron shuttle between cathode and TEA. Studies have revealed that the microbial community can transfer the electrons through one or multiple pathways [180]. Several studies have demonstrated that a variety of substrates can be treated using pure and mixed culture bio-cathodic MFCs [60, 65, 163, 185, 186]. The performance of the bio-cathode can be influenced by the initial catholyte concentration of dissolved oxygen (DO). In one of the recent studies, the PD for nitrogen wastewater treating MFC was highest for anoxic bio-cathode [52]. The uniqueness of the bio-cathodes lies in the variety of microbial communities interacting with the system to achieve the desired goals. Cao et al. [15] developed a photobio-cathode by illuminating the developed bio-cathode to directly fix dissolved CO_2 or bicarbonate as electron acceptor. The MFC utilising the bio-cathode produced 15 folds higher PD than MFC working with the plain carbon cathode with the maximum achieved PD of 750 mW/m^2 [15]. In another study Wang et al. [156], used an air diffusion bio-cathode to accelerate the ORR in MFCs. The study confirmed the improved ORR in MFC with bio-cathode than abiotic MFC with enhanced current and power densities. The study, however, also revealed that the use of bio-cathode decreased the biodiversity within the system [156]. In a very recent study performed by Izadi et al. [64], a gas diffusion bio-cathode was developed for MFC enriched with iron oxidising bacteria. The study reported an enhanced PD of 1.02 W/m^2 compared to that of 0.59 W/m^2 PD produced using Pt catalyst in continuously operated MFC. The study further revealed that the gas

diffusion electrode (GDE) improved the mass transfer and the MFC performance and provided a reproducible and fast startup for bio-cathodic MFC [64]. Like bio-anodes, the activity of the bio-cathodes can be enhanced by modifying the bio-cathode to improve its surface area, biocompatibility and conductivity using appropriate material. Chen et al. [23] developed a microbially in situ synthesised reduced graphene oxide bio-cathode that significantly improved the ORR [23]. Table 1 presents recent advances and modification in electrodes used in MFC and also shown in Fig. 10.

Membrane

Membranes or separators are significantly intrinsic part of MFC physically barring the oxidation and reduction reactions taking place in the anodic and cathodic chambers. In MFC, these separators allow the selective permeation of protons from anodic chamber (where they are produced) to cathodic chamber (where they are consumed). The separators also help in controlling the oxygen diffusion to the anaerobic anodic chamber which could be detrimentally affected by the oxygen penetration [120]. However, the incorporation of the membranes in the MFC system also presents some hurdles like pH splitting caused by the increasing cathodic pH and decreasing anodic pH due to the slow movement of protons from one to the other chamber [87]. Also, the membranes add to the cost of the MFC setup making upto 38% of the capital cost and also increase the internal resistance of the system [49, 58]. A wide variety of materials have been used as separators in MFC like glass wool, ceramics, nanoporous filter, salt bridge and ion exchange membranes (IEMs) [26, 74, 87, 132, 166, 179, 187] beside others. However, the IEMs remain the most widely used separators because of their high conductivity and selective permeability. In MFCs, the most commonly used membranes are the cation exchange membrane (CEMs) or more precisely the proton exchange membranes (PEMs). The positive ions are attracted and permitted to allow through these membranes as they are composed of the backbone of negatively charged groups [120]. Nafion, a fluoropolymer based on sulfonated tetrafluoroethylene group has been widely used in various studies [131]. It has a SO_3^- (sulfonate) group attached to it imparting high proton conductivity. Nafion, however, has the drawbacks of high cost, easily susceptible to biological and chemical biofouling as well as pH splitting [21, 87]. Ghasemi et al. [48] compared the performance of treated, untreated and biofouled Nafion membranes and observed the performance to be following the trend of treated > untreated > biofouled membrane with the CE of the treated membrane being 2.32 and 4.15 times better than untreated and biofouled membranes, respectively [49]. Ultrex is another commonly used PEM. Ultrex CMI-7000 is a strong acid membrane composed of gel polystyrene and divinylbenzene cross-linked polymer with sulphonic acid (SO_3H^-) as the active functional group. Although the membrane is compatible with Nafion in terms of mechanical strength, conductivity and affordability, the higher resistance posed by the membrane lowers its performance [139]. Zirfon, composed of 85:15 wt% of hydrophilic zirconium oxide (ZrO_2) and polysulfone, is an anion exchange membrane (AEM), which outperforms the specific resistance of Nafion membrane and is cheaper. However, it presents a major drawback of high oxygen penetration to the anodic chamber thereby affecting the performance of the MFC system [120, 139].

Table 1 Recent advances and modification in electrodes used in MFC

No	Electrodes used		Substrate	Power density (mW/m^2)	References
	Anode	Cathode			
1	CF	Iron phthalocyanine-MnO_x/CP	Primary clarifier influent	143	Burkitt et al. [13]
2	CB	Cobalt and nitrogen doped carbon	Glucose	1665	You et al. [177]
3	Graphite	Graphite paste-hybrid graphene	Activated sludge/PBS	220	Mashkour et al. [101]
4	CB	3D graphene nanosheets	Sodium acetate	2059	Santoro et al. [129]
5	CC	Iron-nicarbazin/carbon paper	Sodium acetate	1850	Eaktasang et al. [42]
6	CC	V_2O_5/rGO/SS	Fish market wastewater	533	Noori et al. [110]
7	CC	α-MnO_2/GO/AC/CC	Glucose/peptone/yeast	148.4	Tofighi et al. [146]
8	$FeMoO_4$/GP	GP	Sugar industry wastewater	106	Mohamed et al. [107]
9	FeS_2/rGO/CC	GFB	Beer factory waste	310	Wang et al. [154]
10	rGO/MnO_2/CF	CB	Sodium acetate	2065	[183]
11	Brush like PANI nanoarray/CC	CP/Pt	Sodium acetate	567.2	Zhang et al. [187]
12	$MgFe_2O_4$/SS	CP	Congo red/sodium acetate	430.336	Khan et al. [73]
13	Graphene cobalt/nickel composite CC	CP	Glucose	784.89	Li et al. [86]
14	Vertically aligned PANI/CC	CC	Sodium acetate	853	Zhai et al. [181]
15	Tungsten carbide/CC	CB	Sodium acetate	3260	Liu et al. [91]

* CF-carbon felt; CP-carbon paper; CB-carbon brush; CC-carbon cloth; rGO-reduced graphene oxide; SS-stainless steel; GO-graphene oxide; AC-activated carbon; GFB-graphite fibre brush; GP-graphite plate; Pt-platinum

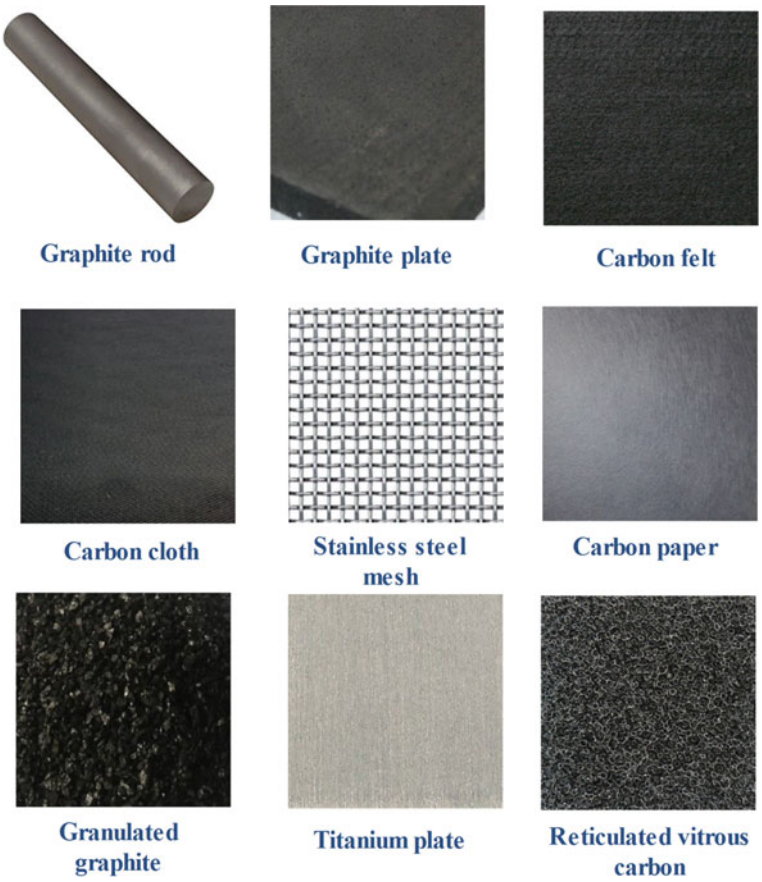

Fig. 10 Commonly used electrodes in MFC

In a very recent study performed by Wang et al. [152], four different IEMs, bipolar exchange membrane (BEM), CEM, PEM and AEM were investigated for chromium removal and electricity generation in MFC. It was observed to follow the trend BPM > AEM > CEM > PEM with PEM displaying pH splitting [152]. San-Martin et al. [128] compared the performances of different commercially available IEMs, Nafion-117, Ultrex CMI-7000, Zirfon Perl UTP and Fumasep FKE and FKB. The study reported Nafion and Ultrex to possess high thermal stability while the other tested membranes displayed better resistance to biofouling. The study further concluded that the electrochemical performance in BES was maintained by all the membranes tested [128]. Verily, an ideal MFC membrane should showcase following characteristics of absolute substrate crossover and oxygen diffusion control, cost-effective with low internal resistance and resistant to biofouling [5]. Recently, novel membrane materials have been synthesised and tested that can possibly be cheaper and perform compatibly with the commercially available membranes. A novel sulphonated polyether ether

ketone membrane (SPEEK) was synthesised and compared for its performance with the Nafion-117 by Ayyaru and Dharmalingam [8]. The study reported the synthesised membrane to display high PD and CE with retarded substrate losses emphasising the potential of electrode in enhancing the performance of MFC system greatly [8]. A polybenzimidazole-based novel PEM has been recently synthesised and tested as a potential separator in MFC and its performance was compared with Nafion-117. The membrane reportedly performed better in terms of power output, durability and treatment efficiency as compared to Nafion. The membrane also showed inhibition to surface bacterial adhesion thus preserving the MFC from biofouling, which is a major drawback with Nafion [5].

4 Biofilm Formation and Microbial Communities Involved in MFC

In order to generate electricity in MFC, the electrons originated by the reduction of organic substrates need to be transferred to the anode, which acts as an electron acceptor. To fulfil this, the electrons are required to be transferred extracellularly. The shuttling of electron between microbes and electrodes is known as extracellular electron transfer (EET) [77]. Potter and Cohen were the first to observe the microbial property of EET in early 1900s. A wide variety of microbial communities have been studied over the years to possess the ability to transfer electrons extracellularly. The microbes performing this process of electron transfer are commonly known as Exoelectrogens. *Geobacter* and *Shewanella* have been the most extensively studied EET performing microbial species. These are gram negative metal-reducing microbes, performing EET via multihaem c-type cytochrome to transfer the electrons to the metals via direct contact [27]. In MFC, these microbes perform the EET to transfer the electrons to anode instead of metal as electron acceptor in the similar fashion. Some widely known examples of exoelectrogens are *Rhodoferax ferrireducen, Shewanella putrefacien, Geobacter sulfurreducen, Geobacter metallireducen* [67]. Wrighton et al. [160] first gave the exoelectrogenic evidence of gram-positive bacteria using *Thermincola potens* strain. Recently, a novel pure culture of gram-positive *P. freudenreichii* was confirmed to behave as exoelectrogen in an H-shaped mediatorless MFC [122]. In a study conducted by Wang et al. [149], *E. coli* was successfully employed to harvest current in MFC with excellent power output of 547 mW/m^2 [149] while [167] isolated *Citrobacter* sp. from MFC as potential exoelectrogen [167]. Studies have suggested mixed culture to be favourable in utilising complex substrates [112]. The electron transport between microbes and electrodes can take place via different routes and has been reported to be broadly categorised in three sections: short-range direct transfer, long-range direct transfer and indirect electron transfer employing special redox-active molecules commonly called mediators to shuttle the electrons between microbes and electron acceptor or

electrode [175]. In MFC start-up, electron transport process to the anode is considered as the rate-limiting step as the biofilm developed on anode plays a crucial role in EET [189]. Four main types of proteins have been identified so far to be involved in EET: Porin-cytochrome complex, a complex of porin and redox protein; surface-bound cytochromes; nanowires; and miscellaneous redox proteins [30, 126]. In case of short-range direct transfer, the physical contact of the developed biofilm with the electrode is a pre-requisite to conduct electron. The microbial community in the biofilm adheres to the electrode and transfer the electrons via the involvement of outer membrane redox multiheme molecules called cytochrome c proteins [69]. In such electron transfer processes, as the physical contact is an important criterion for electron conduction, the microbial community only in the closed proximity/physically adhering to the electron (monolayer) is able to perform electron transport thereby limiting the MFC performance. A study evinced that the outer membrane c-cytochrome, OmcA and MtrC are determining factor for *Shewanella* species to generate electricity [160]. In case of *G. Sulfurreducens*, outer membrane cytochromes OmcE, OmcB, OmcZ and OmcS have been reported to have role in electron transport [27, 126]. In the high current producing bioflms, OmcZ has been observed to play a major role. The homogenously carried electron transport through biofilm involves OmcZ while OmcB moderates the electron transport heterogeneously between biofilm and electrode [78]. OmcF has also been reported to play indirect role in current production without directly influencing electron transfer by regulating the synthesis of appropriate proteins like OmcB, OmcE and OmcS by monitoring the relevant gene transcription [33]. Moreover, it has been reported that the microbial communities in developed biofilm have higher dominance of cytochrome as compared to the lag phase [79].

The long-range direct transfer, on the other hand, is able to conduct electrons from microbes to the electrodes more efficiently and rapidly by the development of an electroactive layer. Unlike short-range transfer, in this case, the electron transport is performed via special pili-like electron carrying structures produced by exoelectrogens like *Geobacter* and *Shewanella* species. These produced filaments allow the electrons to be conducted through a more complex multilayered biofilm without the restriction of physical monolayer contact [78]. The nanowires produced by *Geobacter* sp. are comprised of pili protein that have been reported to have metal-like conductivity because of their structural backbone of aromatic amino acids maintaining pi-pi orbital overlapping for electron delocalisation [30]. On the other, nanowires produced *by Shewanella* sp., unlike *Geobacter* are comprised not of pili but are extension of outer membrane and follow an alternative mechanism of conduction called electron hopping. In this model, the electrons hop along the chain of cytochromes that accounts for the current conduction [77]. It has been reported that the nanowire production by *Geobacter* sp. increases when electrode is used as electron acceptor in MFC. Also the effect of temperature and pH change has been observed to be consistent with metal-like materials [99]. Species like *Shewanella* and *Geobacter* can perform electron conduction via three different modes of mediation through outer membrane cytochrome, nanowires or via self-synthesised electron shuttles or mediators [77]. The electron transfer achieved via mediators is known as indirect

electron transfer or mediated electron transfer [69]. Mediators play a crucial role of electron shuttling between the microbes and the electrodes. Mediator can be divided into two main categories of endogenous and exogenous. An endogenous mediator is a microbial synthesised substance while an exogenous mediator is an externally added redox substance that plays the role of electron shuttle. Endogenous soluble electron mediators are excreted by microbes like *G. fermentas, P. aeruginosa, S. oneidensis* and *L. lactis. G. fermentas* produces riboflavin, *P. aeruginosa* secretes pyocyanin and phanazine-1-carboxamide while *S. oneidensis* synthesise riboflavin and flavin mononucleotide as extracellar mediators [78]. Exogenous electron mediators are utilised by microbial communities like *D. desulfuricans, E. coli, P. fluoroscens, P. vulgaris, P. micorbili*s beside others. Several studies have reported the use of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), redox dyes and ferricyanide as exogenous electron shuttles [69, 191].

Electron flow in MFC can take place bidirectionally: from microbes to electrode (anode) and electrode (cathode) to microbes. Microbial species like *Geobacter* and *Shewanella* can potentially transfer electrons bidirectionally. Moreover, biocommunities like *C. pasteurianum, A. colcoacenticus, A. ferrooxidans* apart from *Geobacter* and *Shewanella* can perform electron transfer from cathode to microbes [27, 77, 78]. The electron transfer mechanism of *Geobacter* in case of cathode to microbe has been reported to be completely different from microbe to anode electron transfer. Periplasm located cytochrome PccH is a potential candidate in cathode to microbe electron transport by *Geobacter*. On the other hand, *Shewanella* has been reported to follow the same electron transfer mechanism involving flavin and riboflavin with c-cytochrome in reverse direction [32, 140]. Methods like chemical, high temperature or surface binding pre-treatment of electrodes and anode modification affect the development of biofilm and thus performance of MFC [77]. CNT/PPy-modified electrode has been reported to enhance the power output from MFC metabolising glucose substrate as a result of better electrode-bacteria interaction on modified electrode [196]. Lui et al. [95] reported PEDOT (poly (3,4-ethylenedioxythiophene) to increase the active sites for bacterial catalytic reactions and improve MFC performance [95]. Further, the addition of biosurfactants like rhamnolipid to anolyte has been recently reported to increase the development of biofilm and electron transfer resulting in an improved MFC performance [189]. Heavy metal ions like Cu^{2+} and Cd^{2+} added to the anodic chamber can potentially enhance the riboflavin electron shuttle synthesis and effectively improved the EET and MFC performance [168]. Figure 11 presents the pictorial representation of various modes of electron transfer.

5 Types of MFC

Various different MFC configurations have been developed over the years in a bid to achieve high and sustainable performance in longer run and at larger scale. The MFC configurations are mainly categorised into two groups: air-cathode MFCs and

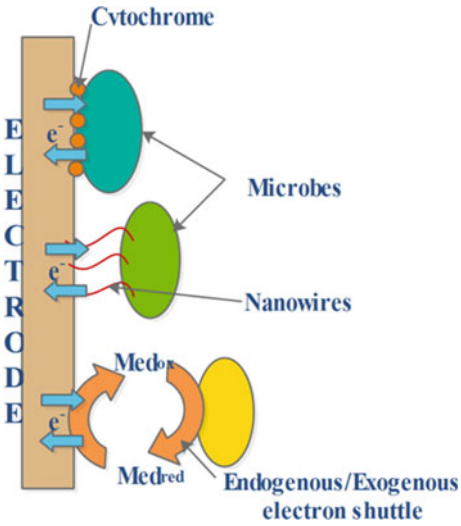

Fig. 11 Pictorial representation of direct and indirect modes of electron transfer

liquid-feed MFCs. The most common MFC configurations are single and dual chambered MFCs. The following section discusses some common MFC configurations developed over the years (Fig. 12).

Single Chambered MFCs (SCMFCs)

This is the most basic configuration of MFC and falls under the category of air-cathode MFC. SCMFC is comprised of a single anodic anaerobic chamber with anode separated through a membrane to an air cathode (placed at outer surface of the reactor). The electrodes are connected using external circuits. The anodic microbial community feeds on the added substrate and release electrons, which flow through the circuit generating electric current. The transported electrons are accepted by oxygen as TEA [39, 69]. SCMFCs have the benefit over dual chambered MFCs of reduced cost of catholyte and aeration as air-cathode MFCs take atmospheric oxygen as TEA [109]. Membrane-less SCMFCs have also been constructed to further lower the operational cost in various studies; however, membrane-less MFCs pose the problem of lower performance because of anodic oxygen diffusion [134, 195].

Dual Chambered MFCs (DCMFCs)

DCMFCs, like SCMFCs are also basic and widely used configuration that mainly falls under the category of liquid feed cathode. DCMFC consists of two separate anaerobic anodic and aerobic cathodic chambers separated by the membrane (mainly PEM) to avoid liquid and oxygen diffusion and allow protons to pass through it to the cathodic chamber. DCMFCs can simultaneously treat two different waste streams in anodic and cathodic chambers respectively (e.g. degradation of organic-rich substrate in anode and metal recovery via reduction in cathode) [69]. Different designs of DCMFC have been developed like H-shaped and rectangular DCMFC [20, 82, 184].

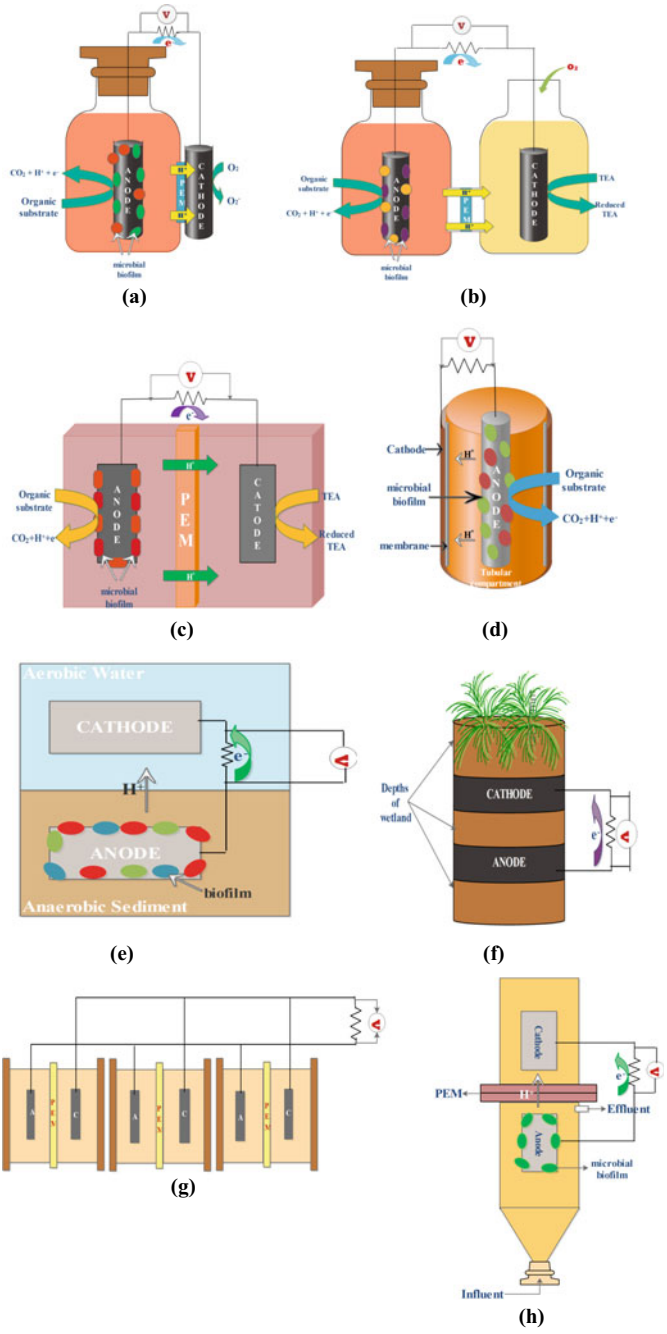

Fig. 12 Various designs of MFC. **a** SCMFC. **b** H-shaped DCMFC. **c** Cubical-DCMFC. **d** Tubular MFC. **e** SMFC. **f** CW-MFC. **g** Stacked MFC. **h** Upflow MFC

Tubular Chambered MFCs

The reactor is mainly a cylindrical single chambered system comprised of a folded membrane surrounded by the cathode/anode. The anodic chamber is inoculated with anaerobic sludge and organic substrate is added. Rabaey et al. [118] constructed a continuous tubular MFC with graphite granules and graphite mat as anode and cathode, respectively. The cathode was dripped over with ferricyanide solution as electron acceptor [118]. Cheng et al. [22] constructed mini air-cathode tubular MFCs to treat benzene contaminated groundwater. The three mini-tubular MFCs were comprised of folded anode surrounded membrane with internal air-cathodes. The systems were dipped in the benzene contaminated water. The results revealed the considerable performance in terms of treatment and power generation [22]. Liao et al. [88] reported a novel method to improve the performance of tubular MFC by employing a rotating carbon brush anode resulting in a dramatic power output of 210 W/m^3 [88]. Tubular MFC has the potential advantage over others of enhanced scalability in continuously operated systems with increased sludge retention and diminished hydraulic retention time thereby reducing the overall operating cost [69, 124].

Up-flow MFCs (UMFC)

He et al. [57] combined the benefits of upflow anaerobic sludge bed reactor (UASB) of long biomass retention and high treatment efficiency to MFC. A UMFC consists of two cylindrical compartments separated by membrane with cathodic compartment located on top of anodic compartment. The anodic feed is allowed to recirculate in the system at defined rate. He et al. treated a common carbohydrate, sucrose to harvest electrical output [57]. Xylose wastewater was treated in an UMFC with AEM and flat graphite electrodes and revealed that decreasing HRT improved the power output at optimum recirculation rate [83]. Recently, single chambered UMFCs have gained attention across globe as a potential approach to reduce the operating cost and high maintenance and difficulty in upscaling and [143] successfully treated Acid orange 7 azo dye in one such single chambered UMFC [143]. Another study demonstrated that the KCl concentration plays an important role in enhancing the anode to cathode electron transfer while chemical oxygen demand (COD) increase has derogatory effect on the voltage recovery as excessive biofilm formation increases the internal resistance [144].

Staked MFCs

The systematic arrangement of individual MFCs in series and parallel pattern is collectively known as stacked MFCs. In this type of configuration, individual fuel cells arrange to form a battery fuel cell. The arrangement does not affect the individual CE of MFC but improves the overall performance of the newly arranged system [69]. Both stacked connections show potential applications in MFC performance with series connection directly affecting the output voltage of the system compared to the individual units. On the other hand, in parallel arrangement voltage stabilisation with enhanced current output is observed [7]. Winfield et al. [158] studied the effect

of electronic configuration on the hydraulically connected MFCs and observed both configurations to improve the output performance compared to the individual cells however, in parallel connection the power and current output were 2 and 10 folds higher than series stack, which was proposed to be result of shunt losses in series stack because of fluidic and electrical connections. One of the biggest drawbacks of stacking is voltage reversal in the connected MFCs as it can severely damage the bio-anode and limit the performance. Voltage reversal has been suggested to be caused by kinetics imbalance at electrodes. To overcome another issue of proton accumulation in the anodic chamber of MFC, hybrid stack of hydraulically connected SC and DC MFCs were constructed. Compared to the individual stacks of SC and DC, the hybrid SC/DC stack was reported to generate higher electric output. The proton accumulation was proposed to be monitored due to the oxygen diffusion through SCMFC cathode to acetate metabolising biofilm [170].

Sediment MFCs (SMFC)

SMFC harvest energy by connecting marine sediments with seawater. They generate energy from anaerobic sediments and aerobic water electropotential difference. To construct a SMFC, anaerobic anode is buried into the sediments and connected to the overlying aerobic cathode. The organic matter in sediments is metabolised by anaerobes and the electrons produced are collected at anode and transported to cathode thereby generating current [69, 194]. The first SMFC was constructed by Reimer and co-workers [123]. Rate of organic loading influence the performance of SMFC. Zhao et al. [193] studied the effect of different organic loading rates on MFC performance and observed that the excess loading can lead to biogas accumulation causing system to break down while the low loading limits the power output [193]. Another study suggested that high polarity organic contaminants are preferably treated in SMFCs [165]. The removal of toxic waste (mercury, silver and zinc) present in the sediments was studied using SMFC and reported to achieve more than 80% removal of all contaminants with successful energy generation [1].

Constructed wetland MFCs (CW-MFCs)

Constructed wetland (CW) is a widely employed wastewater treatment technology allowing the treatment by taking advantages of natural processes like filtration. CW-MFC is an emerging technology capable of harvesting energy while performing waste treatment. The wetlands (CW-MFCs) are constructed by burying anode in the depth and allowing the cathode to be exposed freely to the available oxygen. Anaerobic and aerobic conditions in wetland prevail throughout the depth with anaerobic conditions maintained in the deeper depths and aerobic conditions present at the surface of wetlands from atmospheric oxygen penetration [37]. Plants in wetlands perform filtration and adsorption of wastewater while degradation is performed by anaerobic and aerobic microbes [194]. Araneda et al. [6] performed the treatment of greywater (wastewater generated in households and office buildings) in CW-MFCs with *Phragmites australis* as wetland plant and matrix of gravel achieving the maximum PD of 719.57 mW/m^2 and COD removal efficiency of 91.7% [6].

6 Substrates in MFC

Several kinds of wastewaters have been investigated in MFC to study their treatment and effect on different factors like PD, COD removal and CE. A wide range of wastewaters treated in the MFC can be broadly divided into Defined or Simple Substrate and Undefined or Complex Substrate. MFCs can treat waste both anaerobically in anodic chamber and aerobically in cathodic chamber. In anodic chamber, the substrate added is fed upon by anaerobes and oxidised to yield electrons and protons. Alternatively in the cathodic chamber, the aerobic microbial community transfers the electrons to the externally added TEAs, which are thereby reduced to simpler less harmful products.

Defined or Simple Substrate

Various pure simple organic contaminants have been utilised over the years to harvest electrical output. Carbohydrates, amino acids and volatile fatty acids are the simplest metabolic fuels that make up the more complex waste among which carbohydrates are the most commonly utilised MFC metabolite. These simple metabolites or pure substrates commonly referred to as synthetic wastewater have been tested in MFCs as electron donor to generate electric output. Acetate is the simplest and most commonly used carbon source reported in various MFC studies. Acetate and butyrate have been compared for electric output in a SCMFC and acetate was observed to generate 66% higher power output than butyrate fed MFC [92]. In another study, mechanism of glucose metabolisation in MFC was studied and reported to involve the syntrophic relation of fermenters and electrogens. The fermenters act on glucose to produce hydrogen and acetate which are acted upon by electrogens to produce carbon dioxide, protons and electrons [46]. Catal et al. [17] studied energy generation from 12 monosaccharides including 1 aldonic acid (gluconic acid), 2 uronic acids (glucouronic acid and galacturonic acid), 3 pentoses (arabinose, xylose and ribose) and 6 hexoses (fructose, glucose, galactose, rhamnose, fucose and mannose) using mixed microbial community. The results presented more than 80% COD removal of all monosaccharides. Mannose and glucouronic acid were observed to produce lowest and highest power output, respectively [17]. The results demonstrated a wide range of monosaccharides as potential fuel in MFC for electricity generation. Glucose (fermentable) and acetate (non-fermentable) remain the most evaluated MFC substrate however the lower performance from fermentable substrate compared to non-fermentable substrate has been suggested to be the consequence of denser biofilm metabolising fermentable substrate [112].

Proteins also form an important constituent of wastewater like domestic wastewater. MFC has been studied to harvest electricity from nitrogen-containing wastewater. Cystein, a proteinogenic amino acid has been employed as electron donor in DCMFC [97]. Yang et al. [169] tested eight amino acids namely L-Asparagine, DL-Alanine, L-Aspartic acid, L-Arginine, L-Glutamic acid, L-Histidine, L-lysine and L-Serine as substrate in SCMFC and observed L-Serine and DL-Alanine to generate highest and lowest PD, respectively [169]. In a recent study [82], treated

P-nitroaniline in DCMFC in the presence and absence of co-substrate. The result revealed that both PD and COD removal efficiency decreased as the concentration of P-nitroaniline in anodic chamber increased; however, the addition of co-substrate improved the power output by two folds [82]. In another study, urea as a form of total ammonia nitrogen was successfully treated in SCMFC upto the concentration of 3490 mg/L with more than 80% achievable nitrogen removal. The PD was reported to increased upto 69% on increasing the total ammonia nitrogen concentration from 80 to 3490 mg/L. However, further increase has detrimental effect on MFC performance [153].

Undefined or Complex Substrate

Real wastewater discarded from domestic, municipal, agricultural and industrial sources are not pure but rather complex consisting of variety of treatable components. MFC owing to its ability of treating wastewater with simultaneously harvesting energy has been employed to test a wide range of waste streams. A few of the complex substrates have been discussed in this section. Agro-food waste like brewery, manure, swine and dairy are generally very rich in organic content and show high biodegradability. Dairy wastewater is rich in biodegradable content with sugar making upto 97% of the total COD [112]. It was treated in long run in DCMFC for 2.5 months with successful remediation of high COD substrate achieving a maximum PD of 27 W/m^3 [19]. Swine wastewater has been treated in CW-MFCs while maintaining upflow-downflow scheme. The observed results showed 70 and 75% increase in PD and ammonia removal efficiency compared to the continuous upflow system [38]. Winery wastewater, an important agro-industrial waste is rich in biodegradable organics. Using this wastewater, Pentaedo et al. [114] harvested power output of upto 465 mW/m^2 in a DCMFC [113].

Food waste is referred to the food losses occurring in the food chain. Food waste is mainly rich in carbohydrates. Nearly 1/3rd of the food globally produced per year is lost as waste [84]. Thus, food waste garners a lot of attention for high biodegradability, potential for energy and inexhaustibility. Food waste is disposed from both domestic and commercial sectors and pose serious environmental concerns like odour, toxic gas emission and contamination of groundwater. Goud et al. [51] treated canteen-based food waste in SCMFC and successfully harnessed electrical energy via anaerobic biotreatment. The study revealed that optimum organic loading rate affects the MFC output performance [51]. A similar study performed by Li et al. [84] revealed that the aromatic and hydrophilic fractions of canteen-based food waste were more readily and preferentially degraded than non-aromatic compounds and neutral fractions [84]. In another study, MFC treated orange peel waste to generate PD of 358 mW/m^2 while simultaneously achieving a COD removal efficiency above 80% [105]. Domestic and municipal wastewater have been of major interest among research working in the field of energy recovery. Domestic wastewater can be treated in MFC successfully with upto 80% COD removal and power recovery within a hydraulic retention range of 3–33 h at an influent strength of 50–220 mg/L [93]. Septic wastewater is rich in COD content, which is potentially convertible to useful energy. Yazdi et al. [174] studied the treatment of septic wastewater in stack MFC and obtained the PD of 142

mW/m^2 from three parallel connected units [174]. Urine in another study was used as MFC substrate to generate electric output and simultaneously recover struvite, a phosphate fertiliser present in urine [176].

Further, the decomposition of organic waste and rainwater percolation at landfills sites generates organic constituent rich waste called Landfill Leachate. Landfill Leachate is heavily polluted wastewater that contains organic/inorganic and heavy metal waste capable of heavily contaminating groundwater through percolation. MFC can potentially treat this waste to generate power output. In one of such study, leachate was treated in a SCMFC to obtain a maximum open circuit potential and specific PD of 1.29 V and 1513 mW/m^2. The results also revealed that the volumetric PD increase with increase in surface area while area-specific PD decrease with increase in electrode surface area [135]. Moharir and Tembhurkar [108] studied the effect of recirculating food waste leachate anolyte to generate the highest PD of 29.23 mW/m^2 and achieving COD removal efficiency of 65.76% suggesting an increase in PD and COD removal on anolyte recirculation [108].

Textile industry is one of the largest and most complex industries generating tonns of recalcitrant toxic waste every year that is rich in organic content and a potential resource of energy. Azo dyes are the most commonly used dye (making upto 60%) in textile industry that is extremely toxic, carcinogenic and mutagenic in nature. These factors make textile wastewater a priority candidate among wastewater treatment researchers. MFC has been widely employed in dye treatment. Khan et al. [70] successfully treated two azo dyes viz. Reactive Orange 16 and Acid Navy Blue R in MFC with simultaneous energy recovery [70]. Congo Red has been treated in the presence of 3 different co-substrate (glucose, acetate and ethanol) and observed the highest PD of 103 mW/m^2 with glucose followed by acetate and ethanol respectively [16]. In a recently conducted study, textile effluent and Scarlett RR dye were treated in phytobed MFC with *Chrysopogon zizanioides* and *Typha angustifolia* plants to enhance the COD, TDS and colour reduction [66].

Industrial wastewater is a huge source of contamination to water bodies affecting the biotic communities present in the ecosystem. A collective wastewater sample consisting of waste from chemical, metal, vegetable oil, glass and marble and other industries was treated to produce the maximum voltage output of 890 mV [2]. Other industrial wastewaters treated are rice mill water [10], soak liquor [121], neomycin sulphate antibiotic [18] and surgical cotton industry [141]. A comparative analysis of some common MFC substrates has been presented in Table 2.

7 Terminal Electron Acceptors

In MFCs, electron flow occurs from lower redox potential (anode) to higher redox potential (cathode). The availability of appropriate TEA that overcomes potential losses makes the cell thermodynamically favourable for electron flow. A good TEA reflects the properties of low cost, ease of availability, sustainability in biotic/abiotic environments for prolonged duration, fast kinetics and high redox potential [56]. The

Table 2 Comparative performances of some common substrates using different electrodes

Type of substrate		Anode	Cathode	Membrane	PD (mW/m^2)	References
Acetate		FeS_2/rGO/CC	GFB	CMI 7000	3220	Wang et al. [154]
		GFB	(S-ZrO_2) /CC	–	1079	Iannaci et al. [61]
		CP	CP	Fe_3O_4/PES nanocomposite	9.59	Palma et al. (2018)
Glucose		CC	CC	Nafion-117	123.4	Lin et al. [90]
		Porous carbon/CF	Membrane cathode assembly	–	1606	Chen et al. [24]
		$NiWO_4$/GO/CC	CC/Pt	Nafion-117	1458	Geetanjali et al. (2019)
Domestic wastewater		GFB/CM composite	CB/AC mixture	Textile separator	524	Wu et al. [162]
		CC	CC	Glass wool	62.93	Yang et al. [172]
Distillery water		GP	GP	Nafio-117	63.8	Samsudeen et al. [127]
		CC	CC	PVA/SSA	67.1	Lin et al. [89]
Brewery wastewater		CBr	CBr	CT-PMC	3882	Harewood et al. [55]
		GF	CC/Pt	Polypropylene nanowoven fabric	1519	Yu et al. [178]
Dye waste water	Direct red 80	GF	GC/Pt	Nafion-117	455	Miran et al. [106]
	Brilliant green	GO coated SSM	Chromium Plate	CMI 7000	400	Khalid et al. [68]
Petroleum refinery wastewater		Carbon coated CC	CC/Pt	Nafion-117	225	[137]
		CR	GG/GFl	Nafiom-117	330	Guo et al. [53]
Dairy wastewater		CC	Pt/C	Nafion-117	50	Choudhury et al. [28]
		Cu doped FeO nanoparticle/CP	CP	Nafion-117	162	Sekar et al. [130]
Dark fermentation effluent		CC	CC	Zirfon	165	Elmekawy et al. [41]
		CC	GDE	Zirfon	19.79	Babu et al. [9]

* rGO-reduced graphene oxide; C-carbon; CC-carbon cloth; GFB-Graphite Fibre Brush, CP-carbon paper; PES-polyethersulfone; CF-carbon felt; GO-graphene oxide; Pt- platinum; CM-carbon mesh; CB-carbon black; AC-activated carbon; GP-graphite plate; PVA-polyvinyl alcohol; SSA-sulfosuccinic acid; CBr-carbon brush; CT-chitosan; PMC-poly (malic acid-citric acid); GF-graphite felt; GC-graphite cloth; SSM-stainless steel mesh; CR-carbon rod; GG-graphite granule; GFl-graphite flakes; GDE-gas diffusion electrode

most commonly used TEA in MFC by far is oxygen owing to its easy availability, high redox potential and sustainable nature. However, a wide range of alternate TEAs have been studied in MFCs like dyes, metal ions and others. The TEA employed in MFCs can be broadly divided into inorganic and organic compounds. Oxygen is the most widely used inorganic electron acceptor and has played the role of TEA in various studies [11, 41, 45, 94, 119]. It can be supplied to the electrode by either directly exposing electrode to the air or by aerating the cathodic compartment [147]. Poor oxygen-electrode interaction/contact and slow reduction rate of oxygen on plain carbon-based electrode limit the performance of MFC. The reduction reaction can be improved by modifying carbon electrodes with the help of ORR enhancing catalysts. The redox potential of nitrate is comparable to oxygen making it a potential TEA. Biologically catalysed denitrification was first performed by Clauwaert et al. [29] yielding the power output of 8 W/m^3 and removing upto 0.146 $kgNO_3—Nm^{-3}d^{-1}$ [29]. Wang et al. [151] studied nitrate treatment and suggested that the feed-drain frequency enhances the nitrification-denitrification efficiency [151]. The nitrite accumulation at cathode has been observed as a major issue in denitrification due to its health concern and should be achieved to minimise denitrification. The environmental conditions like pH, DO and insufficient electron donors do not significantly affect the nitrite accumulation. [138] modelled denitrification yielding parameter to design bio-cathode performing higher denitrification [138]. Wu et al. [164] design a novel MFC with aerated electroconductive membrane bio-cathode to improve nitrification-denitrification [164]. Ferricyanide is another popular TEA used in various studies owing to its high redox potential [35, 103]. However, ferricyanide has a disadvantage of frequent chemical regeneration limiting its use as electron acceptor [104]. Several other metal ions have been reduced in MFC like Cr(VI) [54, 76], bromate (BrO_3^-) [31], Fe(III) [80], heavy metal ions like Cu^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Cr^{2+}, SO_4^{2-}, percarbonate (HCO_3^-) and Mn^{7+} [40, 44, 54, 133, 155, 161]. Simultaneous nitrate and perchlorate removal has also been achieved in MFC [65]. *Chlorella*-based bio-cathode has been employed in MFC for Cd^{2+} removal [188]. Buffered catholytes especially PBS has been used in MFCs to maintain pH balance. Saline water has also been studied as potential catholyte [3]. Various organic contaminants have also been employed as TEA in cathode compartment of MFC. A variety of textile dyes have been used as potential electron acceptors and reduced at MFC cathode. Oon et al. [111] successfully employed various mono and diazo dyes as TEA and observed 50% higher decolorisation for mono than diazo dyes [111]. Nitrobenzene, nitrophenol, ethanoamine have also been tested as cathodic electron acceptor generating significant voltage output [191, 192]. Phenol and chlorophenols (CPs) are colourless organic compounds that are potential carcinogens. Khan et al. have explored the bioremediation of these contaminants at cathode in MFCs [71, 72, 74, 75].

8 Challenges

MFC on many fronts has emerged as a technology, which is suitable and sustainable in harvesting energy from waste in an eco-friendly way. Development of commercial prototypes like Cambarian innovation and initiatives of companies like Pilus Energy and Emefcy has brought the technology a step closer to commercialisation. However, issues concerning low power output, electron transfer efficiency or CE, understanding of suitable wastefeed and microbial processes taking place within the system still present challenges in scaling up of the technology. Factors like wastewater concentration, composition, unwanted biomass, side processes like methanogenesis, optimum pH, diffusion across separators, incomplete biodegradation limits the waste treatment in MFC [5].

The efficiency of electrical recovery (CE) is another major concern regarding MFC scaleup. Six major reasons for low CE as suggested by Pandey et al. [88, 112] are:

(a) Electron diversion to non-exoelectrogens.
(b) Substrate consumption by competitive pathways like methanogenesis.
(c) Metabolic inhibition of biomass because of toxicant and proton buildup.
(d) Substrate lockup of electrons.
(e) Low transfer efficiency to/from electrodes.
(f) Inappropriate separators causing electrolyte/oxygen diffusion to the other chamber.

As the interaction of biomass and electrode plays a crucial role in MFC, designing appropriate electrode with high biocompatibility is a major challenge. This chapter has made attempts to discuss the various electrode modification advances made recently to design suitable electrodes that can effectively tackle fouling, corrosion and enhance activity. Further the cost of MFC components is still too high for practical implication and suitable, economically feasible alternatives are much needed to make the technology commercially feasible [9].

9 Conclusion

Water and energy are undoubtedly the most essential contributing factors of the society. As per a Slovakian proverb “Water is the first and foremost medicine” and clean water is the basic right of all living souls inhibiting the earth. Energy on the other hand is a mean to derive the society forward. The continuously growing society with rapid industrialisation has led to one major issue of water contamination making it unfit for daily activities. MFC technology has earned the focus of the world research as a potential technique linking the basic needs of the mankind. It treats wastewater and harvest energy in the form of electric power from the organic/inorganic contaminants. MFC technology promises to be a carbon-neutral clean source of renewable energy.

The article reviews the role of different configurational aspect of MFC on its performance. From the article, it can be concluded that MFC can achieve high performance by optimising the factors such as electrode used, membrane and microbes involved, and selection and concentration of substrates being treated. However, for the practical implementation of this technology, further research in the field of longevity, system fouling, role of internal resistance and microbial kinetics needs to be deeply explored.

Acknowledgements The authors wish to acknowledge Department of Chemistry, Aligarh Muslim University, Aligarh for providing necessary research facilities. Authors are also thankful to Science and Engineering Research Board (SERB), University Grants Commission for departmental research support in the form of DRS II Grant.

References

1. Abbas SZ, Rafatullah M, Khan MA, Siddiqui MR (2019) Bioremediation and electricity generation by using open and closed sediment microbial fuel cells. Front Microbiol 10:1–12. https://doi.org/10.3389/fmicb.2018.03348
2. Abbasi U, Jin W, Pervez A, Bhatti ZA, Tariq M, Shaheen S, Iqbal A, Mahmood Q (2016) Anaerobic microbial fuel cell treating combined industrial wastewater: correlation of electricity generation with pollutants. Bioresour Technol 200:1–7. https://doi.org/10.1016/j.biortech.2015.09.088
3. Ahn Y, Logan BE (2013) Saline catholytes as alternatives to phosphate buffers in microbial fuel cells. Bioresour Technol 132:436–439. https://doi.org/10.1016/j.biortech.2013.01.113
4. An BM, Song YH, Shin JW, Park JY (2016) Two-chamber microbial fuel cell to simultaneously remove ethanolamine and nitrate. Desalin Water Treat 57:7866–7873. https://doi.org/10.1080/19443994.2015.1083482
5. Angioni S, Millia L, Bruni G, Ravelli D, Mustarelli P, Quartarone E (2017) Novel composite polybenzimidazole-based proton exchange membranes as efficient and sustainable separators for microbial fuel cells. J Power Sour 348:57–65. https://doi.org/10.1016/j.jpowsour.2017.02.084
6. Araneda I, Tapia NF, Allende KL, Vargas IT (2018) Constructed wetland-microbial fuel cells for sustainable greywater treatment. Water (Switzerland) 10:1–9. https://doi.org/10.3390/w10070940
7. Asensio Y, Mansilla E, Fernandez-Marchante CM, Lobato J, Cañizares P, Rodrigo MA (2017) Towards the scale-up of bioelectrogenic technology: stacking microbial fuel cells to produce larger amounts of electricity. J Appl Electrochem 47:1115–2112. https://doi.org/10.1007/s10800-017-1101-2
8. Ayyaru S, Dharmalingam S (2011) Development of MFC using sulphonated polyether ether ketone (SPEEK) membrane for electricity generation from waste water. Bioresour Technol 102:11167–11171. https://doi.org/10.1016/j.biortech.2011.09.021
9. Babu S, Srikanth S, Mohan SV, Pant D (2015) Continuous mode operation of microbial fuel cell (MFC) stack with dual gas diffusion cathode design for the treatment of dark fermentation effluent. Int J Hydrog Energy 40:12424–12435. https://doi.org/10.1016/j.ijhydene.2015.07.049
10. Behera M, Jana PS, More TT, Ghangrekar MM (2010) Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH. Bioelectrochemistry 79:228–233. https://doi.org/10.1016/j.bioelechem.2010.06.002

11. Biffinger JC, Pietron J, Ray R, Little B, Ringeisen BR (2007) A biofilm enhanced miniature microbial fuel cell using Shewanella oneidensis DSP10 and oxygen reduction cathodes. Biosens Bioelectron 22:1672–1679. https://doi.org/10.1016/j.bios.2006.07.027
12. Buitrón G, Moreno-Andrade I (2014) Performance of a single-chamber microbial fuel cell degrading phenol: effect of phenol concentration and external resistance. Appl Biochem Biotechnol 174:2471–2481. https://doi.org/10.1007/s12010-014-1195-5
13. Burkitt R, Whiffen TR, Yu EH (2016) Iron phthalocyanine and MnOx composite catalysts for microbial fuel cell applications. Appl Catal B Environ 181:279–288. https://doi.org/10.1016/j.apcatb.2015.07.010
14. Cai H, Wang J, Bu Y, Zhong Q (2013) Treatment of carbon cloth anodes for improving power generation in a dual-chamber microbial fuel cell. J Chem Technol Biotechnol 88:623–628. https://doi.org/10.1002/jctb.3875
15. Cao X, Huang X, Liang P, Boon N, Fan M, Zhang L, Zhang X (2009) A completely anoxic microbial fuel cell using a photo-biocathode for cathodic carbon dioxide reduction. Energy Environ Sci 2:498–501. https://doi.org/10.1039/b901069f
16. Cao Y, Hu Y, Sun J, Hou B (2010) Explore various co-substrates for simultaneous electricity generation and Congo red degradation in air-cathode single-chamber microbial fuel cell. Bioelectrochemistry 79:71–76. https://doi.org/10.1016/j.bioelechem.2009.12.001
17. Catal T, Li K, Bermek H, Liu H (2008) Electricity production from twelve monosaccharides using microbial fuel cells. J Power Sour 175:196–200. https://doi.org/10.1016/j.jpowsour.2007.09.083
18. Catal T, Yavaser S, Enisoglu-Atalay V, Bermek H, Ozilhan S (2018) Monitoring of neomycin sulfate antibiotic in microbial fuel cells. Bioresour Technol 268:116–120. https://doi.org/10.1016/j.biortech.2018.07.122
19. Cecconet D, Molognoni D, Callegari A, Capodaglio AG (2018) Agro-food industry wastewater treatment with microbial fuel cells: energetic recovery issues. Int J Hydrog Energy 43:500–511. https://doi.org/10.1016/j.ijhydene.2017.07.231
20. Cetinkaya AY, Ozkaya B, Taskan E, Karadag D, Cakmakci M (2016) The production of electricity from dual-chambered microbial fuel cell fueled by old age leachate. Energy Sour Part A Recov Util Environ Eff 38:1544–1552. https://doi.org/10.1080/15567036.2013.843041
21. Chae KJ, Choi M, Ajayi FF, Park W, Chang IS, Kim IS (2008) Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells. Energy Fuels 22:169–176. https://doi.org/10.1021/ef700308u
22. Chang SH, Wu CH, Wang RC, Lin CW (2017) Electricity production and benzene removal from groundwater using low-cost mini tubular microbial fuel cells in a monitoring well. J Environ Manag 193:551–557. https://doi.org/10.1016/j.jenvman.2017.02.053
23. Chen J, Hu Y, Huang W, Zhang L (2017) Enhanced electricity generation for biocathode microbial fuel cell by in situ microbial-induced reduction of graphene oxide and polarity reversion. Int J Hydrog Energy 42:12574–12582. https://doi.org/10.1016/j.ijhydene.2017.03.012
24. Chen X, Cui D, Wang X, Wang X, Li W (2015) Porous carbon with de fi ned pore size as anode of microbial fuel cell. Biosens Bioelectron 69:135–141. https://doi.org/10.1016/j.bios.2015.02.014
25. Cheng S, Logan BE (2007) Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. Electrochem Commun 9:492–496. https://doi.org/10.1016/j.elecom.2006.10.023
26. Cheraghipoor M, Mohebbi-Kalhori D, Noroozifar M, Maghsoodlou MT (2021) Production of greener energy in microbial fuel cell with ceramic separator fabricated using native soils: effect of lattice and porous SiO_2. Fuel 284:118938
27. Choi O, Sang BI (2016) Extracellular electron transfer from cathode to microbes: application for biofuel production. Biotechnol Biofuels 9:1–14. https://doi.org/10.1186/s13068-016-0426-0
28. Choudhury P, Ray RN, Bandyopadhyay TK, Basak B, Muthuraj M, Bhunia B (2021) Process engineering for stable power recovery from dairy wastewater using microbial fuel cell. Int J Hydrog Energy 46(4):3171–3182

29. Clauwaert P, Rabaey K, Aelterman P, De SL, Pham TH, Boeckx P, Boon N, Vrestraete W (2007) Biological denitrification in microbial fuel cells. Environ Sci Technol 41:3354–3360
30. Costa NL, Clarke TA, Philipp LA, Gescher J, Louro RO, Paquete CM (2018) Electron transfer process in microbial electrochemical technologies: the role of cell-surface exposed conductive proteins. Bioresour Technol 255:308–317. https://doi.org/10.1016/j.biortech.2018.01.133
31. Dai H, Yang H, Liu X, Zhao Y, Liang Z (2016) Performance of sodium bromate as cathodic electron acceptor in microbial fuel cell. Bioresour Technol 202:220–225. https://doi.org/10.1016/j.biortech.2015.12.008
32. Dantas JM, Campelo LM, Duke NEC, Salgueiro CA, Pokkuluri PR (2015) The structure of PccH from Geobacter sulfurreducens—A novel low reduction potential monoheme cytochrome essential for accepting electrons from an electrode. FEBS J 282:2215–2231. https://doi.org/10.1111/febs.13269
33. Dantas JM, Silva MA, Pantoja-Uceda D, Turner DL, Bruix M, Salgueiro CA (2017) Solution structure and dynamics of the outer membrane cytochrome OmcF from Geobacter sulfurreducens. Biochim Biophys Acta Bioenerg 1858:733–741. https://doi.org/10.1016/j.bbabio.2017.03.007
34. Das I, Noori MT, Bhowmick GD, Ghangrekar MM (2018) Synthesis of bimetallic iron ferrite $Co0.5Zn0.5Fe_2O_4$ as a superior catalyst for oxygen reduction reaction to replace noble metal catalysts in microbial fuel cell. Int J Hydrog Energy 43:19196–19205. https://doi.org/10.1016/j.ijhydene.2018.08.113
35. Deeke A, Sleutels THJA, Hamelers HVM, Buisman CJN (2012) Capacitive bioanodes enable renewable energy storage in microbial fuel cells. Environ Sci Technol 46:3554–3560
36. Di Palma L, Bavasso I, Sarasini F, Tirillò J, Puglia D, Dominici F, Torre L (2018) Synthesis, characterization and performance evaluation of Fe_3O_4/PES nano composite membranes for microbial fuel cell. Eur Polym J 99:222–229. https://doi.org/10.1016/j.eurpolymj.2017.12.037
37. Doherty L, Zhao Y, Zhao X, Hu Y, Hao X, Xu L, Liu R (2015) A review of a recently emerged technology: constructed wetland—Microbial fuel cells. Water Res 85:38–45. https://doi.org/10.1016/j.watres.2015.08.016
38. Doherty L, Zhao Y, Zhao X, Wang W (2015) Nutrient and organics removal from swine slurry with simultaneous electricity generation in an alum sludge-based constructed wetland incorporating microbial fuel cell technology. Chem Eng J 266:74–81. https://doi.org/10.1016/j.cej.2014.12.063
39. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25:464–482. https://doi.org/10.1016/j.biotechadv.2007.05.004
40. Eaktasang N, Kang CS, Lim H, Kwean OS, Cho S, Kim Y, Kim HS (2016) Production of electrically-conductive nanoscale filaments by sulfate-reducing bacteria in the microbial fuel cell. Bioresour Technol 210:61–67. https://doi.org/10.1016/j.biortech.2015.12.090
41. Elmekawy A, Srikanth S, Vanbroekhoven K, De WH, Pant D (2014) Bioelectro-catalytic valorization of dark fermentation effluents by acetate oxidizing bacteria in bioelectrochemical system (BES). J Power Sour 262:183–191. https://doi.org/10.1016/j.jpowsour.2014.03.111
42. Erable B, Oliot M, Lacroix R, Bergel A, Serov A, Kodali M, Santoro C, Atanassov P (2018) Iron-Nicarbazin derived platinum group metal-free electrocatalyst in scalable-size air-breathing cathodes for microbial fuel cells. Electrochim Acta 277:127–135. https://doi.org/10.1016/j.electacta.2018.04.190
43. Feng Y, Yang Q, Wang X, Logan BE (2010) Treatment of carbon fiber brush anodes for improving power generation in air—cathode microbial fuel cells. J Power Sour 195:1841–1844. https://doi.org/10.1016/j.jpowsour.2009.10.030
44. Forrestal C, Huang Z, Ren ZJ (2014) Percarbonate as a naturally buffering catholyte for microbial fuel cells. Bioresour Technol 172:429–432. https://doi.org/10.1016/j.biortech.2014.09.014
45. Freguia S, Rabaey K, Yuan Z, Keller J (2007) Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells. Electrochim Acta 53:598–603. https://doi.org/10.1016/j.electacta.2007.07.037

46. Freguia S, Rabaey K, Yuan Z, Keller J (2008) Syntrophic processes drive the conversion of glucose in microbial fuel cell anodes. Environ Sci Technol 42:7937–7943
47. Geetanjali, Rani R, Sharma D, Kumar S (2019) Optimization of operating conditions of miniaturize single chambered microbial fuel cell using NiWO4/graphene oxide modified anode for performance improvement and microbial communities dynamics. Bioresour Technol 285:121337. https://doi.org/10.1016/j.biortech.2019.121337
48. Ghasemi M, Daud WRW, Hassan SHA, Oh SE, Ismail M, Rahimnejad M, Jahim JM (2013) Nano-structured carbon as electrode material in microbial fuel cells: a comprehensive review. J Alloys Compd 580:245–255. https://doi.org/10.1016/j.jallcom.2013.05.094
49. Ghasemi M, Wan Daud WR, Ismail M, Rahimnejad M, Ismail AF, Leong JX, Miskan M, Ben Liew K (2013) Effect of pre-treatment and biofouling of proton exchange membrane on microbial fuel cell performance. Int J Hydrog Energy 38:5480–5484. https://doi.org/10.1016/j.ijhydene.2012.09.148
50. Goel M, Chovelon JM, Ferronato C, Bayard R, Sreekrishnan TR (2010) The remediation of wastewater containing 4-chlorophenol using integrated photocatalytic and biological treatment. J Photochem Photobiol B Biol 98:1–6. https://doi.org/10.1016/j.jphotobiol.2009.09.006
51. Goud RK, Babu PS, Mohan SV (2011) Canteen based composite food waste as potential anodic fuel for bioelectricity generation in single chambered microbial fuel cell (MFC): bioelectrochemical evaluation under increasing substrate loading condition. Int J Hydrog Energy 36:6210–6218. https://doi.org/10.1016/j.ijhydene.2011.02.056
52. Guo J, Cheng J, Li B, Wang J, Chu P (2019) Performance and microbial community in the biocathode of microbial fuel cells under different dissolved oxygen concentrations. J Electroanal Chem 833:433–440. https://doi.org/10.1016/j.jelechem.2018.12.015
53. Guo X, Zhan Y, Chen C, Cai B, Wang Y, Guo S (2016) Influence of packing material characteristics on the performance of microbial fuel cells using petroleum refinery wastewater as fuel. Renew Energy 87:437–444. https://doi.org/10.1016/j.renene.2015.10.041
54. Habibul N, Hu Y, Wang Y, Chen W, Yu H, Sheng G (2016) Bioelectrochemical Chromium (VI) removal in plant-microbial fuel cells. Environ Sci Technol 50:3882–3889. https://doi.org/10.1021/acs.est.5b06376
55. Harewood AJT, Popuri SR, Cadogan EI, Lee C-H, Wang C-C (2017) Bioelectricity generation from brewery wastewater in a microbial fuel cell using chitosan/biodegradable copolymer membrane. Int J Environ Sci Technol 14:1535–1550. https://doi.org/10.1007/s13762-017-1258-6
56. He CS, Mu ZX, Yang HY, Wang YZ, Mu Y, Yu HQ (2015) Electron acceptors for energy generation in microbial fuel cells fed with wastewaters: a mini-review. Chemosphere 140:99–105. https://doi.org/10.1016/j.chemosphere.2015.03.059
57. He Z, Minteer SD, Angenent LT (2005) Electricity generation from artificial wastewater using an upflow microbial fuel cell. Environ Sci Technol 39:5262–5267. https://doi.org/10.1021/es0502876
58. Hernández-Flores G, Poggi-Varaldo HM, Solorza-Feria O (2016) Comparison of alternative membranes to replace high cost Nafion ones in microbial fuel cells. Int J Hydrog Energy 41:23354–23362. https://doi.org/10.1016/j.ijhydene.2016.08.206
59. Hirooka K, Ichihashi O, Takeguchi T (2018) Sodium cobalt oxide as a non-platinum cathode catalyst for microbial fuel cells. Sustain Environ Res 28:322–325. https://doi.org/10.1016/j.serj.2018.07.002
60. Hsu L, Masuda SA, Nealson KH, Pirbazari M (2012) Evaluation of microbial fuel cell Shewanella biocathodes for treatment of chromate contamination. RSC Adv 2:5844–5855. https://doi.org/10.1039/c2ra20478a
61. Iannaci A, Sciarria TP, Mecheri B, Adani F, Licoccia S, Epifanio AD (2017) Power generation using a low–cost sulfated zirconium oxide based cathode in single chamber microbial fuel cells. J Alloys Compd 693:170–176. https://doi.org/10.1016/j.jallcom.2016.09.159
62. International Energy Agency F (2017) World gross electricity production, by source
63. International Energy Agency F (2019) World Energy Outlook 2019

64. Izadi P, Fontmorin JM, Fernández LFL, Cheng S, Head I, Yu EH (2019) High performing gas diffusion biocathode for microbial fuel cells using acidophilic iron oxidizing bacteria. Front Energy Res 7:1–10. https://doi.org/10.3389/fenrg.2019.00093
65. Jiang C, Yang Q, Wang D, Zhong Y, Chen F, Li X, Zeng G, Li X, Shang M (2017) Simultaneous perchlorate and nitrate removal coupled with electricity generation in autotrophic denitrifying biocathode microbial fuel cell. Chem Eng J 308:783–790. https://doi.org/10.1016/j.cej.2016.09.121
66. Kadam SK, Watharkar AD, Chandanshive VV, Khandare RV, Jeon BH, Jadhav JP, Govindwar SP (2018) Co-planted floating phyto-bed along with microbial fuel cell for enhanced textile effluent treatment. J Clean Prod 203:788–798. https://doi.org/10.1016/j.jclepro.2018.08.336
67. Kashima H, Regan JM (2015) Facultative nitrate reduction by electrode-respiring Geobacter metallireducens biofilms as a competitive reaction to electrode reduction in a bioelectrochemical system. Environ Sci Technol 49:3195–3202. https://doi.org/10.1021/es504882f
68. Khalid S, Alvi F, Fatima M, Aslam M, Riaz S, Farooq R, Zhang Y (2018) Dye degradation and electricity generation using microbial fuel cell with graphene oxide modified anode. Mater Lett 220:272–276. https://doi.org/10.1016/j.matlet.2018.03.054
69. Khan MD, Khan N, Sultana S, Joshi R, Ahmed S, Yu E, Scott K, Ahmad A, Khan MZ (2017) Bioelectrochemical conversion of waste to energy using microbial fuel cell technology. Process Biochem 57:141–158. https://doi.org/10.1016/j.procbio.2017.04.001
70. Khan MZ, Singh S, Sultana S, Sreekrishnan TR, Ahammad SZ (2015) Studies on the biodegradation of two different azo dyes in bioelectrochemical systems. New J Chem 39:5597–5604. https://doi.org/10.1039/C5NJ00541H
71. Khan N, Anwer AH, Ahmad A, Sabir S, Khan MZ (2020) Investigating microbial fuel cell aided bio-remediation of mixed phenolic contaminants under oxic and anoxic environments. Biochem Eng J 155:107485
72. Khan N, Anwer AH, Ahmad A, Sabir S, Sevda S, Khan MZ (2019) Investigation of CNT/PPy-modified carbon paper electrodes under anaerobic and aerobic conditions for phenol bioremediation in microbial fuel cells. ACS Omega 5(1):471–480
73. Khan N, Anwer AH, Khan MD, Azam A, Ibhadon A, Khan MZ (2021) Magnesium ferrite spinels as anode modifier for the treatment of Congo red and energy recovery in a single chambered microbial fuel cell. J Hazard Mater 410:124561
74. Khan N, Khan MD, Ansari MY, Ahmad A, Khan MZ (2019) Bio-electrodegradation of 2,4,6-trichlorophenol by mixed microbial culture in dual chambered microbial fuel cells. J Biosci Bioeng 127:353–359. https://doi.org/10.1016/j.jbiosc.2018.08.012
75. Khan N, Khan MD, Nizami AS, Rehan M, Shaida MA, Ahmad A, Khan MZ (2018) Energy generation through bioelectrochemical degradation of pentachlorophenol in microbial fuel cell. RSC Adv 8(37):20726–20736
76. Kim C, Lee CR, Song YE, Heo J, Choi SM, Lim DH, Cho J, Park C, Jang M, Kim JR (2017) Hexavalent chromium as a cathodic electron acceptor in a bipolar membrane microbial fuel cell with the simultaneous treatment of electroplating wastewater. Chem Eng J 328:703–707. https://doi.org/10.1016/j.cej.2017.07.077
77. Kumar A, Hsu LHH, Kavanagh P, Barrière F, Lens PNL, Lapinsonnière L, Lienhard JH, Schröder U, Jiang X, Leech D (2017) The ins and outs of microorganism-electrode electron transfer reactions. Nat Rev Chem 1:1–13. https://doi.org/10.1038/s41570-017-0024
78. Kumar R, Singh L, Wahid ZA, Din MFM (2015) Exoelectrogens in microbial fuel cells toward bioelectricity generation: a review. Int J Energy Res 39:1048–1067. 10.1002/er
79. Kumar R, Singh L, Zularisam AW, Hai FI (2018) Microbial fuel cell is emerging as a versatile technology: a review on its possible applications, challenges and strategies to improve the performances. Int J Energy Res 42:369–394. https://doi.org/10.1002/er.3780
80. Kumar SS, Malyan SK, Bishnoi NR (2017) Performance of buffered ferric chloride as terminal electron acceptor in dual chamber microbial fuel cell. J Environ Chem Eng 5:1238–1243. https://doi.org/10.1016/j.jece.2017.02.010
81. Lai B, Tang X, Li H, Du Z, Liu X, Zhang Q (2011) Power production enhancement with a polyaniline modified anode in microbial fuel cells. Biosens Bioelectron 28:373–377. https://doi.org/10.1016/j.bios.2011.07.050

82. Lai C, Li B, Chen M, Zeng G, Huang D, Qin L, Liu X, Cheng M, Wan J, Du C, Huang F, Liu S, Yi H (2018) Simultaneous degradation of P-nitroaniline and electricity generation by using a microfiltration membrane dual-chamber microbial fuel cell. Int J Hydrog Energy 43:1749–1757. https://doi.org/10.1016/j.ijhydene.2017.11.025
83. Lay CH, Kokko ME, Puhakka JA (2015) Power generation in fed-batch and continuous up-flow microbial fuel cell from synthetic wastewater. Energy 91:235–241. https://doi.org/10.1016/j.energy.2015.08.029
84. Li H, Tian Y, Zuo W, Zhang J, Pan X, Li L, Su X (2016) Electricity generation from food wastes and characteristics of organic matters in microbial fuel cell. Bioresour Technol 205:104–110. https://doi.org/10.1016/j.biortech.2016.01.042
85. Li J, Liu G, Zhang R, Luo Y, Zhang C, Li M (2010) Electricity generation by two types of microbial fuel cells using nitrobenzene as the anodic or cathodic reactants. Bioresour Technol 101:4013–4020. https://doi.org/10.1016/j.biortech.2009.12.135
86. Li L, Liu S, Wang H, Yang P (2018) Application of graphene-cobalt/nickel composite-carbon cloth modified electrode in microbial fuel cell. Environ Eng Sci 35:1173–1184. https://doi.org/10.1089/ees.2017.0543
87. Li WW, Sheng GP, Liu XW, Yu HQ (2011) Recent advances in the separators for microbial fuel cells. Bioresour Technol 102:244–252. https://doi.org/10.1016/j.biortech.2010.03.090
88. Liao Q, Zhang J, Li J, Ye D, Zhu X, Zhang B (2015) Increased performance of a tubular microbial fuel cell with a rotating carbon-brush anode. Biosens Bioelectron 63:558–561. https://doi.org/10.1016/j.bios.2014.08.014
89. Lin C, Wu C, Huang W, Tsai S (2015) Evaluation of different cell-immobilization strategies for simultaneous distillery wastewater treatment and electricity generation in microbial fuel cells. Fuel 144:1–8. https://doi.org/10.1016/j.fuel.2014.12.009
90. Lin T, Bai X, Hu Y, Li B, Yuan Y, Song H (2017) Synthetic Saccharomyces cerevisiae-Shewanella oneidensis consortium enables glucose-fed high-performance microbial fuel cell. Am Inst Chem Eng 63:1830–1838. https://doi.org/10.1002/aic
91. Liu D, Chang Q, Gao Y, Huang W, Sun Z, Yan M, Guo C (2020) High performance of microbial fuel cell afforded by metallic tungsten carbide decorated carbon cloth anode. Electrochim Acta 330:135243. https://doi.org/10.1016/j.electacta.2019.135243
92. Liu H, Cheng S, Logan BE (2005) Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. Environ Sci Technol 39:658–662. https://doi.org/10.1021/es048927c
93. Liu H, Ramnarayanan R, Logan BE (2004) Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol 38:2281–2285. https://doi.org/10.1021/es034923g
94. Liu S, Feng X, Gu F, Li X, Wang Y (2017) Sequential reduction/oxidation of azo dyes in a three-dimensional biofilm electrode reactor. Chemosphere 186:287–294
95. Liu X, Wu W, Gu Z (2015) Poly (3,4-ethylenedioxythiophene) promotes direct electron transfer at the interface between Shewanella loihica and the anode in a microbial fuel cell. J Power Sour 277:110–115. https://doi.org/10.1016/j.jpowsour.2014.11.129
96. Logan BE, Hamelers B, Rozendal R, Schroder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40:5181–5192. https://doi.org/10.1021/es0605016
97. Logan BE, Murano C, Scott K, Gray ND, Head IM (2005) Electricity generation from cysteine in a microbial fuel cell. Water Res 39:942–952. https://doi.org/10.1016/j.watres.2004.11.019
98. Majidi MR, Shahbazi Farahani F, Hosseini M, Ahadzadeh I (2019) Low-cost nanowired α-MnO_2/C as an ORR catalyst in air-cathode microbial fuel cell. Bioelectrochemistry 125:38–45. https://doi.org/10.1016/j.bioelechem.2018.09.004
99. Malvankar NS, Lovley DR (2014) Microbial nanowires for bioenergy applications. Curr Opin Biotechnol 27:88–95. https://doi.org/10.1016/j.copbio.2013.12.003
100. Mao C, Feng Y, Wang X, Ren G (2015) Review on research achievements of biogas from anaerobic digestion. Renew Sustain Energy Rev 45:540–555. https://doi.org/10.1016/j.rser.2015.02.032

101. Mashkour M, Rahimnejad M, Pourali SM, Ezoji H, ElMekawy A, Pant D (2017) Catalytic performance of nano-hybrid graphene and titanium dioxide modified cathodes fabricated with facile and green technique in microbial fuel cell. Prog Nat Sci Mater Int 27:647–651. https://doi.org/10.1016/j.pnsc.2017.11.003
102. Mecheri B, Iannaci A, D'Epifanio A, Mauri A, Licoccia S (2016) Carbon-supported zirconium oxide as a cathode for microbial fuel cell applications. ChemPlusChem 81:80–85. https://doi.org/10.1002/cplu.201500347
103. Mehdinia A, Ziaei E, Jabbari A (2014) Multi-walled carbon nanotube/SnO_2 nanocomposite: a novel anode material for microbial fuel cells. Electrochim Acta 130:512–518. https://doi.org/10.1016/j.electacta.2014.03.011
104. Mink JE, Hussain MM (2013) Sustainable design of high- performance microsized microbial fuel cell with carbon nanotube anode and air cathode. ACS Nano 7:6921–6927
105. Miran W, Nawaz M, Jang J, Lee DS (2016) Conversion of orange peel waste biomass to bioelectricity using a mediator-less microbial fuel cell. Sci Total Environ 547:197–205. https://doi.org/10.1016/j.scitotenv.2016.01.004
106. Miran W, Rasool K, Nawaz M, Kadam A, Shin S, Heo J, Jang J, Lee S (2016) Simultaneous electricity production and direct red 80 degradation using a dual chamber microbial fuel cell. Desalin Water Treat 57:9051–9059. https://doi.org/10.1080/19443994.2015.1049410
107. Mohamed SN, Thomas N, Tamilmani J, Boobalan T, Matheswaran M, Kalaichelvi P, Alagarsamy A, Pugazhendhi A (2020) Bioelectricity generation using iron (II) molybdate nanocatalyst coated anode during treatment of sugar wastewater in microbial fuel cell. Fuel 277:118119
108. Moharir PV, Tembhurkar AR (2018) Effect of recirculation on bioelectricity generation using microbial fuel cell with food waste leachate as substrate. Int J Hydrog Energy 43:10061–10069. https://doi.org/10.1016/j.ijhydene.2018.04.072
109. Munoz-Cupa C, Hu Y, Xu C, Bassi A (2021) An overview of microbial fuel cell usage in wastewater treatment, resource recovery and energy production. Sci Total Environ 754:142429
110. Noori MT, Mukherjee CK, Ghangrekar MM (2017) Enhancing performance of microbial fuel cell by using graphene supported V_2O_5-nanorod catalytic cathode. Electrochim Acta 228:513–521. https://doi.org/10.1016/j.electacta.2017.01.016
111. Oon YS, Ong SA, Ho LN, Wong YS, Oon YL, Lehl HK, Thung WE, Nordin N (2017) Microbial fuel cell operation using monoazo and diazo dyes as terminal electron acceptor for simultaneous decolourisation and bioelectricity generation. J Hazard Mater 325:170–177. https://doi.org/10.1016/j.jhazmat.2016.11.074
112. Pandey P, Shinde VN, Deopurkar RL, Kale SP, Patil SA, Pant D (2016) Recent advances in the use of different substrates in microbial fuel cells toward wastewater treatment and simultaneous energy recovery. Appl Energy 168:706–723. https://doi.org/10.1016/j.apenergy.2016.01.056
113. Penteado ED, Fernandez-Marchante CM, Zaiat M, Cañizares P, Gonzalez ER, Rodrigo MAR (2016) Energy recovery from winery wastewater using a dual chamber microbial fuel cell. J Chem Technol Biotechnol 91:1802–1808. https://doi.org/10.1002/jctb.4771
114. Penteado ED, Fernandez-Marchante CM, Zaiat M, Gonzalez ER, Rodrigo MA (2017) On the effects of ferricyanide as cathodic mediator on the performance of microbial fuel cells. Electrocatalysis 8:59–66. https://doi.org/10.1007/s12678-016-0334-x
115. Pinto D, Coradin T, Laberty-Robert C (2018) Effect of anode polarization on biofilm formation and electron transfer in Shewanella oneidensis/graphite felt microbial fuel cells. Bioelectrochemistry 120:1–9. https://doi.org/10.1016/j.bioelechem.2017.10.008
116. Pu K-B, Ma Q, Cai WF, Chen Q-Y, Wang YH, Li F-J (2018) Polypyrrole modified stainless steel as high performance anode of microbial fuel cell. Biochem Eng J 132:255–261. https://doi.org/10.1016/j.bej.2018.01.018
117. Qiao Y, Li CM, Bao SJ, Bao QL (2007) Carbon nanotube/polyaniline composite as anode material for microbial fuel cells. J Power Sour 170:79–84. https://doi.org/10.1016/j.jpowsour.2007.03.048

118. Rabaey K, Clauwaert P, Aelterman P, Verstraete W (2005) Tubular microbial fuel cells for efficient electricity generation. Environ Sci Technol 39:8077–8082
119. Rabaey K, Read ST, Clauwaert P, Freguia S, Bond PL, Blackall LL, Keller J (2008) Cathodic oxygen reduction catalyzed by bacteria in microbial fuel cells. ISME J 2:519–527. https://doi.org/10.1038/ismej.2008.1
120. Rahimnejad M, Adhami A, Darvari S, Zirepour A, Oh S-E (2015) Microbial fuel cell as new technology for bioelectricity generation: a review. Alex Eng J. https://doi.org/10.1016/j.aej.2015.03.031
121. Rajeswari S, Vidhya S, Krishnaraj RN, Saravanan P, Sundarapandiyan S, Maruthamuthu S, Ponmariappan S, Vijayan M (2016) Utilization of soak liquor in microbial fuel cell. Fuel 181:148–156. https://doi.org/10.1016/j.fuel.2016.04.121
122. Reiche A, Sivell J lynn, Kirkwood KM (2016) Electricity generation by Propionibacterium freudenreichii in a mediatorless microbial fuel cell. Biotechnol Lett 38:51–55. https://doi.org/10.1007/s10529-015-1944-8
123. Reimers CE, Girguis P, Stecher HA, Tender LM, Ryckelynck N, Whaling P (2006) Microbial fuel cell energy from an ocean cold seep. Geobiology 4:123–136. https://doi.org/10.1111/j.1472-4669.2006.00071.x
124. Rinaldi A, Mecheri B, Garavaglia V, Licoccia S, Di Nardo P, Traversa E (2008) Engineering materials and biology to boost performance of microbial fuel cells: a critical review. Energy Environ Sci 1:417–429. https://doi.org/10.1039/b806498a
125. Rittmann BE (2008) Opportunities for renewable bioenergy using microorganisms. Biotechnol Bioeng 100:203–212. https://doi.org/10.1002/bit.21875
126. Rotaru AE, Shrestha PM, Liu F, Markovaite B, Chen S, Nevin KP, Lovley DR (2014) Direct interspecies electron transfer between Geobacter metallireducens and Methanosarcina barkeri. Appl Environ Microbiol 80:4599–4605. https://doi.org/10.1128/AEM.00895-14
127. Samsudeen N, Radhakrishnan TK, Matheswaran M (2015) Bioelectricity production from microbial fuel cell using mixed bacterial culture isolated from distillery wastewater. Bioresour Technol 195:242–247. https://doi.org/10.1016/j.biortech.2015.07.023
128. San-Martín MI, Carmona FJ, Alonso RM, Prádanos P, Morán A, Escapa A (2019) Assessing the ageing process of cation exchange membranes in bioelectrochemical systems. Int J Hydrog Energy 44:25287–25296. https://doi.org/10.1016/j.ijhydene.2019.08.004
129. Santoro C, Kodali M, Kabir S, Soavi F, Serov A, Atanassov P (2017) Three-dimensional graphene nanosheets as cathode catalysts in standard and supercapacitive microbial fuel cell. J Power Sour 356:371–380. https://doi.org/10.1016/j.jpowsour.2017.03.135
130. Sekar AD, Jayabalan T, Muthukumar H, Chandrasekaran NI, Mohamed SN, Matheswaran M (2019) Enhancing power generation and treatment of dairy waste water in microbial fuel cell using Cu-doped iron oxide nanoparticles decorated anode. Energy 172:173–180. https://doi.org/10.1016/j.energy.2019.01.102
131. Selvaraj D, Somanathan A, Jeyakumar R, Kumar G (2020) Generation of electricity by the degradation of electro-Fenton pretreated latex wastewater using double chamber microbial fuel cell. Int J Energy Res 44(15):12496–12505
132. Sevda S, Dominguez-Benetton X, Graichen FHM, Vanbroekhoven K, De WH, Sreekrishnan TR, Pant D (2016) Shift to continuous operation of an air-cathode microbial fuel cell long-running in fed-batch mode boosts power generation. Int J Green Energy 13:71–79. https://doi.org/10.1080/15435075.2014.909363
133. Shen J, Huang L, Zhou P, Quan X, Puma GL (2017) Correlation between circuital current, Cu (II) reduction and cellular electron transfer in EAB isolated from Cu (II)-reduced biocathodes of microbial fuel cells. Bioelectrochemistry 114:1–7. https://doi.org/10.1016/j.bioelechem.2016.11.002
134. Sirinutsomboon B (2014) Modeling of a membraneless single-chamber microbial fuel cell with molasses as an energy source. Int J Energy Environ Eng 5:1–9. https://doi.org/10.1007/s40095-014-0093-5
135. Sonawane JM, Adeloju SB, Ghosh PC (2017) Landfill leachate: a promising substrate for microbial fuel cells. Int J Hydrog Energy 42:23794–23798. https://doi.org/10.1016/j.ijhydene.2017.03.137

136. Song R-B, Zhao C-E, Jiang L-P, Abdel-halim ES, Zhang J-R, Zhu J-J (2016) Bacteria-affinity 3D macroporous graphene/MWCNTs/Fe_3O_4 foams for high-performance microbial fuel cells. ACS Appl Mater Interfaces 8:16170–16177. https://doi.org/10.1021/acsami.6b03425
137. Srikanth S, Kumar M, Singh D, Singh MP, Das BP (2016) Electro-biocatalytic treatment of petroleum refinery wastewater using microbial fuel cell (MFC) in continuous mode operation. Bioresour Technol 221:70–77. https://doi.org/10.1016/j.biortech.2016.09.034
138. Srinivasan V, Weinrich J, Butler C (2016) Nitrite accumulation in a denitrifying biocathode microbial fuel cell. Environ Sci Water Res Technol 2:344–352. https://doi.org/10.1039/c5ew00260e
139. Srinophakun P, Thanapimmetha A, Plangsri S, Vetchayakunchai S, Saisriyoot M (2017) Application of modified chitosan membrane for microbial fuel cell: roles of proton carrier site and positive charge. J Clean Prod 142:1274–1282. https://doi.org/10.1016/j.jclepro.2016.06.153
140. Sydow A, Krieg T, Mayer F, Schrader J, Holtmann D (2014) Electroactive bacteria—Molecular mechanisms and genetic tools. Appl Microbiol Biotechnol 98:8481–8495. https://doi.org/10.1007/s00253-014-6005-z
141. Tamilarasan K, Banu JR, Jayashree C, Yogalakshmi KN, Gokulakrishnan K (2017) Effect of organic loading rate on electricity generating potential of upflow anaerobic microbial fuel cell treating surgical cotton industry wastewater. J Environ Chem Eng 5:1021–1026. https://doi.org/10.1016/j.jece.2017.01.025
142. Tang X, Ng HY (2017) Anthraquinone-2-sulfonate immobilized to conductive polypyrrole hydrogel as a bioanode to enhance power production in microbial fuel cell. Bioresour Technol 244:452–455. https://doi.org/10.1016/j.biortech.2017.07.189
143. Thung WE, Ong SA, Ho LN, Wong YS, Ridwan F, Oon YL, Oon YS, Lehl HK (2015) A highly efficient single chambered up-flow membrane-less microbial fuel cell for treatment of azo dye Acid Orange 7-containing wastewater. Bioresour Technol 197:284–288. https://doi.org/10.1016/j.biortech.2015.08.078
144. Thung WE, Ong SA, Ho LN, Wong YS, Ridwan F, Oon YL, Oon YS, Lehl HK (2018) Sustainable green technology on wastewater treatment: the evaluation of enhanced single chambered up-flow membrane-less microbial fuel cell. J Environ Sci (China) 66:295–300. https://doi.org/10.1016/j.jes.2017.05.010
145. Tiwari BR, Ghangrekar MM (2018) Electricity production during distillery wastewater treatment in a microbial fuel cell equipped with low cost PVA-nafion-borosilicate membrane. J Clean Energy Technol, 6:155–158. https://doi.org/10.18178/jocet.2018.6.2.452
146. Tofighi A, Rahimnejad M, Ghorbani M (2019) Ternary nanotube α-MnO_2/GO/AC as an excellent alternative composite modifier for cathode electrode of microbial fuel cell. J Therm Anal Calorim 135:1667–1675. https://doi.org/10.1007/s10973-018-7198-7
147. Ucar D, Zhang Y, Angelidaki I (2017) An overview of electron acceptors in microbial fuel cells. Front Microbiol 8:1–14. https://doi.org/10.3389/fmicb.2017.00643
148. United Nations (2019) Water facts-UN water, pp 1–14
149. Wang CT, Chen WJ, Huang RY (2010) Influence of growth curve phase on electricity performance of microbial fuel cell by Escherichia coli. Int J Hydrog Energy 35:7217–7223. https://doi.org/10.1016/j.ijhydene.2010.01.038
150. Wang D, Ma Z, Xie Y, Zhang M, Zhao N, Song H (2018) Fe/N-doped graphene with rod-like CNTs as an air-cathode catalyst in microbial fuel cells. RSC Adv 8:1203–1209. https://doi.org/10.1039/c7ra11613f
151. Wang H, Liu J, He W, Qu Y, Li D, Feng Y (2016) Energy-positive nitrogen removal from reject water using a tide-type biocathode microbial electrochemical system. Bioresour Technol 222:317–325. https://doi.org/10.1016/j.biortech.2016.09.090
152. Wang H, Song X, Zhang H, Tan P, Kong F (2020) Removal of hexavalent chromium in dual-chamber microbial fuel cells separated by different ion exchange membranes. J Hazard Mater 384:121459. https://doi.org/10.1016/j.jhazmat.2019.121459
153. Wang L, Xie B, Gao N, Min B, Liu H (2017) Urea removal coupled with enhanced electricity generation in single-chambered microbial fuel cells. Environ Sci Pollut Res 24:20401–20408. https://doi.org/10.1007/s11356-017-9689-7

154. Wang R, Yan M, Li H, Zhang L, Peng B, Sun J, Liu D, Liu S (2018) FeS_2 nanoparticles decorated graphene as microbial-fuel-cell anode achieving high power density. Adv Mater 30:1–7. https://doi.org/10.1002/adma.201800618
155. Wang X, Li J, Wang Z, Tursun H, Liu R, Gao Y, Li Y (2016) Increasing the recovery of heavy metal ions using two microbial fuel cells operating in parallel with no power output. Environ Sci Pollut Res 23:20368–20377. https://doi.org/10.1007/s11356-016-7045-y
156. Wang Z, Zheng Y, Xiao Y, Wu S, Wu Y, Yang Z, Zhao F (2013) Analysis of oxygen reduction and microbial community of air-diffusion biocathode in microbial fuel cells. Bioresour Technol 144:74–79. https://doi.org/10.1016/j.biortech.2013.06.093
157. Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85:849–860. https://doi.org/10.1007/s00253-009-2246-7
158. Winfield J, Ieropoulos I, Greenman J (2012) Investigating a cascade of seven hydraulically connected microbial fuel cells. Bioresour Technol 110:245–250. https://doi.org/10.1016/j.biortech.2012.01.095
159. World Health Organization (2019) Fact sheet on drinking water. World Health Organization, Geneva. https://www.who.int/en/news-room/fact-sheets/detail/drinking-water
160. Wrighton KC, Thrash JC, Melnyk RA, Bigi JP, Byrne-Bailey KG, Remis JP, Schichnes D, Auer M, Chang CJ, Coates JD (2011) Evidence for direct electron transfer by a gram-positive bacterium isolated from a microbial fuel cell. Appl Environ Microbiol 77:7633–7639. https://doi.org/10.1128/AEM.05365-11
161. Wu MS, Xu X, Zhao Q, Wang ZY (2017) Simultaneous removal of heavy metals and biodegradation of organic matter with sediment microbial fuel cells. RSC Adv 7:53433–53438. https://doi.org/10.1039/c7ra11103g
162. Wu S, He W, Yang W, Ye Y, Huang X, Logan BE (2017) Combined carbon mesh and small graphite fiber brush anodes to enhance and stabilize power generation in microbial fuel cells treating domestic wastewater. J Power Sour 356:348–355. https://doi.org/10.1016/j.jpowsour.2017.01.041
163. Wu X, Ren X, Owens G, Brunetti G, Zhou J, Yong X, Wei P, Jia H (2018) A facultative electroactive chromium (VI)-reducing bacterium aerobically isolated from a biocathode microbial fuel cell. Front Microbiol 9:1–10. https://doi.org/10.3389/fmicb.2018.02883
164. Wu Y, Yang Q, Zeng Q, Ngo HH, Guo W, Zhang H (2017) Enhanced low C/N nitrogen removal in an innovative microbial fuel cell (MFC) with electroconductivity aerated membrane (EAM) as biocathode. Chem Eng J 316:315–322. https://doi.org/10.1016/j.cej.2016.11.141
165. Xia C, Xu M, Liu J, Guo J, Yang Y (2015) Sediment microbial fuel cell prefers to degrade organic chemicals with higher polarity. Bioresour Technol 190:420–423. https://doi.org/10.1016/j.biortech.2015.04.072
166. Xu L, Zhao Y, Tang C, Doherty L (2018) Influence of glass wool as separator on bioelectricity generation in a constructed wetland-microbial fuel cell. J Environ Manag 207:116–123. https://doi.org/10.1016/j.jenvman.2017.11.035
167. Xu S, Liu H (2011) New exoelectrogen Citrobacter sp. SX-1 isolated from a microbial fuel cell. J Appl Microbiol 111:1108–1115. https://doi.org/10.1111/j.1365-2672.2011.05129.x
168. Xu YS, Zheng T, Yong XY, Zhai DD, Si RW, Li B, Yu YY, Yong YC (2016) Trace heavy metal ions promoted extracellular electron transfer and power generation by Shewanella in microbial fuel cells. Bioresour Technol 211:542–547. https://doi.org/10.1016/j.biortech.2016.03.144
169. Yang Q, Wang X, Feng Y, Lee H, Liu J, Shi X, Qu Y, Ren N (2012) Electricity generation using eight amino acids by air-cathode microbial fuel cells. Fuel 102:478–482. https://doi.org/10.1016/j.fuel.2012.04.020
170. Yang W, Li J, Ye D, Zhang L, Zhu X, Liao Q (2016) A hybrid microbial fuel cell stack based on single and double chamber microbial fuel cells for self-sustaining pH control. J Power Sour 306:685–691. https://doi.org/10.1016/j.jpowsour.2015.12.073
171. Yang W, Wang X, Rossi R, Logan BE (2020) Low-cost Fe–N–C catalyst derived from Fe (III)-chitosan hydrogel to enhance power production in microbial fuel cells. Chem Eng J 380:122522. https://doi.org/10.1016/j.cej.2019.122522

172. Yang Z, Pei H, Hou Q, Jiang L, Zhang L, Nie C (2018) Algal biofilm-assisted microbial fuel cell to enhance domestic wastewater treatment: nutrient, organics removal and bioenergy production. Chem Eng J 332:277–285. https://doi.org/10.1016/j.cej.2017.09.096
173. Yazdi AA, D'Angelo L, Omer N, Windiasti G, Lu X, Xu J (2016) Carbon nanotube modification of microbial fuel cell electrodes. Biosens Bioelectron 85:536–552. https://doi.org/10.1016/j.bios.2016.05.033
174. Yazdi H, Liliana A-G, Ren ZJ (2015) Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production. Bioresour Technol 180:258–263. https://doi.org/10.1016/j.biortech.2014.12.100
175. Yong XY, Yan ZY, Shen HB, Zhou J, Wu XY, Zhang LJ, Zheng T, Jiang M, Wei P, Jia HH, Yong YC (2017) An integrated aerobic-anaerobic strategy for performance enhancement of Pseudomonas aeruginosa-inoculated microbial fuel cell. Bioresour Technol 241:1191–1196. https://doi.org/10.1016/j.biortech.2017.06.050
176. You J, Greenman J, Melhuish C, Ieropoulos I (2016) Electricity generation and struvite recovery from human urine using microbial fuel cells. J Chem Technol Biotechnol 91:647–654. https://doi.org/10.1002/jctb.4617
177. You S, Gong X, Wang W, Qi D, Wang X, Chen X, Ren N (2016) Enhanced cathodic oxygen reduction and power production of microbial fuel cell based on noble-metal-free electrocatalyst derived from metal-organic frameworks. Adv Energy Mater 6:1–9. https://doi.org/10.1002/aenm.201501497
178. Yu J, Park Y, Kim B, Lee T (2015) Power densities and microbial communities of brewery wastewater-fed microbial fuel cells according to the initial substrates. Bioprocess Biosyst Eng 38:85–92. https://doi.org/10.1007/s00449-014-1246-x
179. Yu Y, Ndayisenga F, Yu Z, Zhao M, Lay CH, Zhou D (2019) Co-substrate strategy for improved power production and chlorophenol degradation in a microbial fuel cell. Int J Hydrog Energy 44:20312–20322. https://doi.org/10.1016/j.ijhydene.2019.05.221
180. Yuan H, Hou Y, Abu-Reesh IM, Chen J, He Z (2016) Oxygen reduction reaction catalysts used in microbial fuel cells for energy-efficient wastewater treatment: a review. Mater Horizons 3:382–401. https://doi.org/10.1039/c6mh00093b
181. Zhai DD, Fang Z, Jin H, Hui M, Kirubaharan CJ, Yu YY, Yong YC (2019) Vertical alignment of polyaniline nanofibers on electrode surface for high-performance microbial fuel cells. Bioresour Technol 288:121499. https://doi.org/10.1016/j.biortech.2019.121499
182. Zhang B, Jiang Y, Han J (2017) A flexible nanocomposite membrane based on traditional cotton fabric to enhance performance of microbial fuel cell. Fibers Polym 18:1296–1303. https://doi.org/10.1007/s12221-017-7191-y
183. Zhang C, Liang P, Yang X, Jiang Y, Bian Y, Chen C, Zhang X, Huang X (2016) Binder-free graphene and manganese oxide coated carbon felt anode for high-performance microbial fuel cell. Biosens Bioelectron 81:32–38. https://doi.org/10.1016/j.bios.2016.02.051
184. Zhang F, He Z (2012) Simultaneous nitrification and denitrification with electricity generation in dual-cathode microbial fuel cells. J Chem Technol Biotechnol 87:153–159. https://doi.org/10.1002/jctb.2700
185. Zhang G, Zhao Q, Jiao Y, Wang K, Lee DJ, Ren N (2012) Biocathode microbial fuel cell for efficient electricity recovery from dairy manure. Biosens Bioelectron 31:537–543. https://doi.org/10.1016/j.bios.2011.11.036
186. Zhang L, Fu G, Zhang Z (2019) Simultaneous nutrient and carbon removal and electricity generation in self-buffered biocathode microbial fuel cell for high-salinity mustard tuber wastewater treatment. Bioresour Technol 272:105–113. https://doi.org/10.1016/j.biortech.2018.10.012
187. Zhang W, Xie B, Yang L, Liang D, Zhu Y, Liu H (2017) Brush-like polyaniline nanoarray modified anode for improvement of power output in microbial fuel cell. Bioresour Technol 233:291–295. https://doi.org/10.1016/j.biortech.2017.02.124
188. Zhang Y, He Q, Xia L, Li Y, Song S (2018) Algae cathode microbial fuel cells for cadmium removal with simultaneous electricity production using nickel foam/graphene electrode. Biochem Eng J 138:179–187. https://doi.org/10.1016/j.bej.2018.07.021

189. Zhang Y, Jiang J, Zhao Q, Gao YZ, Wang K, Ding J, Yu H, Yao Y (2017) Accelerating anodic biofilms formation and electron transfer in microbial fuel cells: Role of anionic biosurfactants and mechanism. Bioelectrochemistry 117:48–56. https://doi.org/10.1016/j.bioelechem.2017.06.002
190. Zhang Y, Mo G, Li X, Zhang W, Zhang J, Ye J, Huang X, Yu C (2011) A graphene modified anode to improve the performance of microbial fuel cells. J Power Sour 196:5402–5407. https://doi.org/10.1016/j.jpowsour.2011.02.067
191. Zhang Y, Sun J, Hou B, Hu Y (2011) Performance improvement of air-cathode single-chamber microbial fuel cell using a mesoporous carbon modified anode. J Power Sour 196:7458–7464. https://doi.org/10.1016/j.jpowsour.2011.05.004
192. Zhao F, Rahunen N, Varcoe JR, Chandra A, Avignone-rossa C, Thumser AE (2008) Activated carbon cloth as anode for sulfate removal in a microbial fuel cell. Environ Sci Technol 42:4971–4976
193. Zhao Q, Li R, Ji M, Ren ZJ (2016) Organic content influences sediment microbial fuel cell performance and community structure. Bioresour Technol 220:549–556. https://doi.org/10.1016/j.biortech.2016.09.005
194. Zhao Q, Yu H, Zhang W, Kabutey FT, Jiang J, Zhang Y, Wang K, Ding J (2017) Microbial fuel cell with high content solid wastes as substrates: a review. Front Environ Sci Eng 11:13. https://doi.org/10.1007/s11783-017-0918-6
195. Zhu G, Onodera T, Tandukar M, Pavlostathis SG (2013) Simultaneous carbon removal, denitrification and power generation in a membrane-less microbial fuel cell. Bioresour Technol 146:1–6. https://doi.org/10.1016/j.biortech.2013.07.032
196. Zou Y, Xiang C, Yang L, Sun L, Xu F, Cao Z (2008) A mediatorless microbial fuel cell using polypyrrole coated carbon nanotubes composite as anode material. Int J Hydrog Energy 33:4856–4862. https://doi.org/10.1016/j.ijhydene.2008.06.061

Modern Challenges and Future Perspective of Microbial Fuel Cells

Rahul Sarma and Biraj Kumar Kakati

Abstract Climate change, global warming, and depletion of fossil fuels have become the most imminent crisis which is leading humanity to focus on renewable sources of energy production. The excessive dependence on conventional fuel-based power generation must be tackled by non-depletable green resources. In recent times, Microbial Fuel Cell (MFC) technology has received considerable attention for power generation due to its mild operating conditions and use of a wide range of biodegradable raw materials as substrates. It provides the ability to generate electrical energy from the chemical energy stored in the organic substrate without any intermediate stages, hence avoiding the entropic losses. The direct conversion by the catalytic reaction of naturally occurring microbes makes MFC more feasible and desirable to bring it into practical use. Despite its ease of conversion, the technology is still in the lab-based developing stage. Various bottlenecks including the internal and external losses, high cost of materials, low power output, etc. are the major cause of its hindrance in commercialization. This chapter provides an attempt to comprehensively bring forward the various challenges and future perspectives in the field of MFC. It entails the investigations of numerous factors that influence the bioelectricity generation of MFC such as microorganisms and substrate used, electrode material, membrane, and various operating conditions. The losses associated with the MFC have also been thoroughly examined. Furthermore, this chapter highlights the advancement of MFC by reviewing its advantages and potential applications in the coming years. It also incorporates several prospective for MFC commercialization and scaled-up industrial usage options in the future.

R. Sarma · B. K. Kakati (✉)
Department of Energy, Tezpur University, Tezpur 784 028, India
e-mail: bkakati@tezu.ernet.in; biraj@outlook.com

A. Ahmad et al. (eds.), *Microbial Fuel Cells for Environmental Remediation*,
Sustainable Materials and Technology,
https://doi.org/10.1007/978-981-19-2681-5_19

1 Introduction

The global energy consumption has skyrocketed exponentially in the last few decades with approximately 4.6% increase in 2021 alone. Most of the energy demand is fulfilled by the conventional fossil fuels. The new report from International Energy Agency states the rise in global electricity demand by 5% in the year 2021 [1, 2]. Nobel Laureate (Physics 2021) Giorgio Parisi mentioned climate change as a 'huge threat' to humanity and is very important for the world to take action as quickly as possible. New and alternative methods of energy/electricity production with an approach to net-zero carbon emission have been the need of the hour. With human interventions, innovation, and research the problem of high energy demand, as well as climate change, can be tackled in coming years. Solar, wind, and hydro are some of the high-cost renewable sources which are primarily being used to tackle the issue of the depletion of fossil fuel for power generation [3]. The conversion of chemical energy into electrical energy using a conventional fuel cell has been an uptrending technology [4]. The major advantages fuel cell technology possess are high efficiency, devoid of rotational equipment, non-emission of toxic inorganic oxides like CO_2, NO_x, SO_x, etc. [5].

However, the technology based on biomass can be further explored and scaled up for commercial use with proper implications. The concept of the generation of electricity by the use of organic matter and with the help of microbial activity has been known for ages [6]. Microbial Fuel Cell (MFC) is one of the potential renewable source alternatives. The operating process of MFC is quite similar to that of the conventional fuel cell. MFC is a bio-electrochemical device that converts the chemical energy present in the biomass into electrical energy through the catalytic reaction with the help of microorganisms. The decomposition of organic matter by the bacteria results in the generation of electrons which can be collected through the external circuit [7]. The breakthrough in microbial fuel cells was brought by MC Potter between 1910 and 1911 [8]. The author experienced electron generation using bacterial species like *Escherichia coli* and Saccharomyces with the platinum electrode. The most fascinating roles of bacterias (Geobacteraceae, *Shewanella putrefaciens*, *Rhodoferax ferrireducens*) to release electrons outside their cell can be witnessed in MFC. Such bacteria are called exoelectrogens and are the most essential components [9].

MFC holds various advantages. It allows direct conversion from chemical to electrical energy which results in high conversion efficiency. A wide range of substrates can be used in this system. Moreover, its operation can be carried out at ambient and room temperature without artificial external conditions [10]. Substantial research has been conducted in this field but there remain various challenges that act as a hindrance in its performance, commercialization, and scaling up process. The strengths, weaknesses, threats, and associated opportunities of MFC are summarized in Fig. 1. This chapter provides a comprehensive overview of the various modern constraints in microbial fuel cells and the future perspective of it.

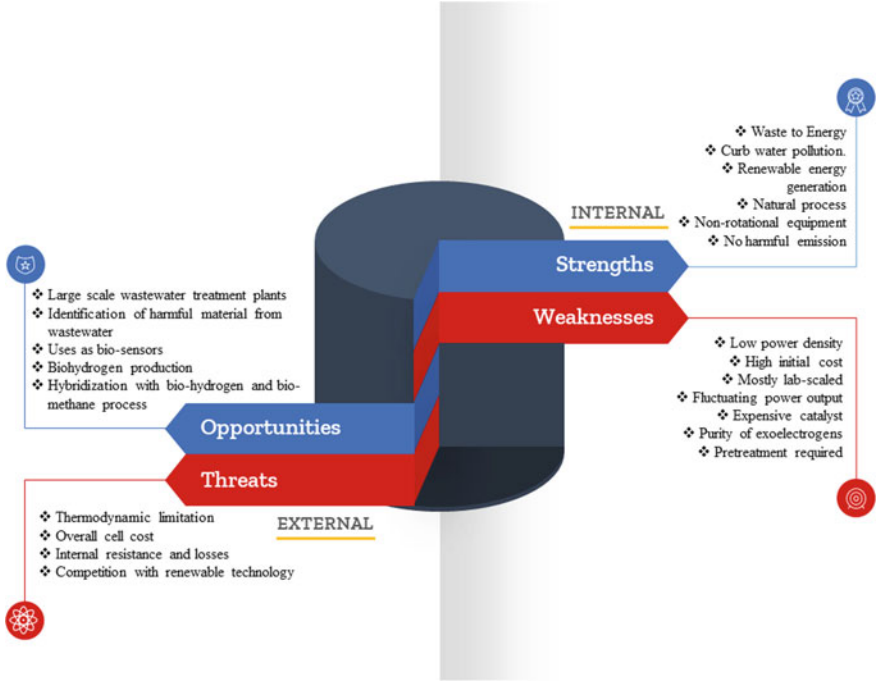

Fig. 1 Strength, weakness, threat, and opportunities of a conventional MFC

2 Working Principle

A typical dual-chambered MFC consists of two chambers (Anodic and cathodic) which consist of two electrodes (anode and cathode) separated by a cation exchange membrane (CEM). In an anodic chamber, the decomposition of the carbon-rich organic substrate takes place. The microbes utilize the raw material in an anaerobic condition, resulting in the release of high energy electrons (e^-) and protons (H^+). Figure 2 depicts the working of an MFC. The electrons are collected through an external circuit and in contrast to that the protons are allowed to pass through the CEM. The reduction reaction takes place at the cathodic chamber leading to the recombination of the protons and electrons to form water, in presence of the atmospheric oxygen [11]. The working formula with sucrose-based lignocellulosic raw material helps to understand the fundamental working of MFC.

At Anode:

$$C_{12}H_{22}O_{11} + 13H_2O \xrightarrow{\text{In presence of bacteria}} 12CO_2 + 48H^+ + 48e^- \quad (1)$$

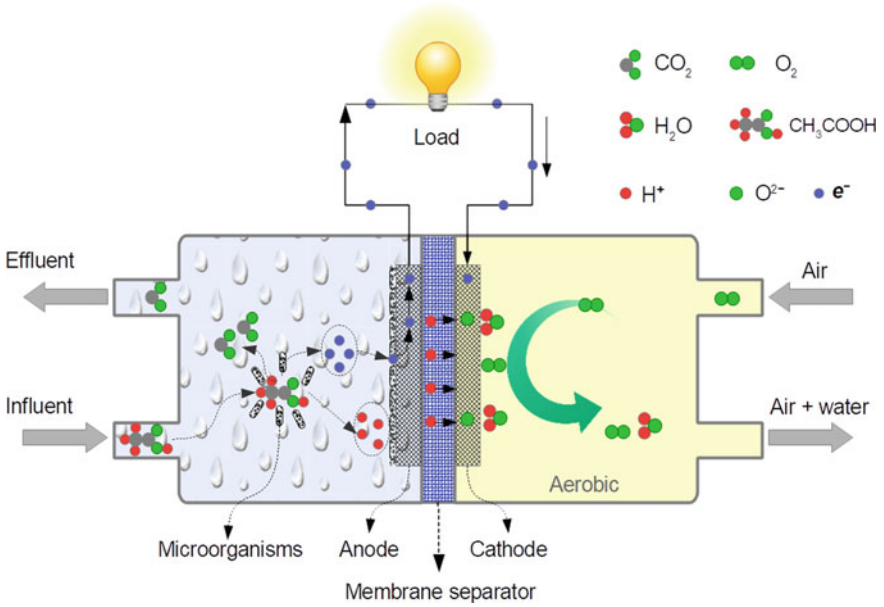

Fig. 2 Working principle of a MFC with CH_3OOH as the main component in the influent waste

At Cathode:

$$48H^+ + 48e^- + 12O_2 \rightarrow 24H_2O \tag{2}$$

The electrons from the cell of the bacteria are transferred to the electrode through three different mechanisms. Firstly, direct contact of the bacterial cell over the surface of the anode. This does not include any mediators and thus can have a columbic efficiency as high as 80% [12]. Secondly through the use of the external mediators which carry the electrons from the microbial cell and assist it to reach the electrode. The need for these mediators is mainly to improve the performance of the MFC and to overcome the problem of non-conductive lipid membrane formation in some of the bacteria [13]. Lastly, electrons are transferred through small thread-like conductive appendages called pilis or nanowires. Bacteria like *Geobacter*, *Shewanella sp.*, etc. are supported through these special features over their cells [14]. The major focus of the researchers on MFC has been to improve electrical performance and limit its various challenges.

3 Factors Affecting the Performance of MFC

The performance of an MFC is mainly focused on effective degradation of the organic matter by the microorganisms as well as the electricity generation [15]. Numerous internal steps are involved, starting from substate input to electron collection in an MFC, where the possibilities of various flaws can be observed. This may include the microorganisms and substrate used, ionic concentration of the medium, electrodes and membrane material used as well as various operating conditions like temperature, pH of the medium, etc. [16].

3.1 Microorganisms Used

Microorganisms, particularly exoelectrogens, are of fundamental importance in the biodegradation and energy generation processes in MFCs. Their catabolism is the major rate-limiting step [17]. Typically, two kinds of bacterias are popular in MFC: the ones that need external mediators like *Escherichia coli, Actinobacillus succinogenes*, *Saccharomyces cerevisiae,* etc. and the other which itself can shuttle the electrons without any means of mediators like *Shewanella putrefaciens, Rhodoferax ferrireducens*, *Geobacter,* etc. [15].

Up to previous decades, only a few microbe species like *Shewanella putrefaciens* were known to be useful in the field of MFC. Researchers now are more interested in the use of mixed cultures as the inoculum. In a study, it is found that the use of mixed cultures is more advantageous than the pure culture because of their nutritional flexibility and stress resilience thus results in higher electricity generation [18]. At the same time, the mixed cultured bacterial species are easily available in wastewater, soil, sludges, dung, etc. The other advantage found in the same research by using the mixed culture is that once the initialization of the metabolism of degrading the substrate occurs by fermentative or methanogenic bacterias (suppose), only one kind of exoelectrogens is sufficient to transfer the electrons generated to the electrode. Some of the challenges in using the mixed culture are non-conductive microbes get adhered on the surface of the electrodes which increases the overall resistance, the start-up time for the current generation is higher and the electroactive biofilm formation on the surface of the anode takes more time [19]. Tables 1 and 2 show the performance of the various mixed and pure bacterial cultures.

3.2 Substrate Used

The substrate or organic material utilized in the anodic chamber is the most important characteristic to consider when evaluating the performance of a microbial fuel cell. A wide range of substrates has been used in MFC which may vary from basic molecules

Table 1 Pure cultured bacteria as inoculum for MFC

Sl. No	Type of bacterial species	Substrate	Reactor design	Power density	References
1.	*Geobacter sulfurreducens*	Acetate	Single chambered, air-cathode	461 mW/m^2	Ishii et al. [20]
2.	*Shewanella putrefaciens*	Lactate	Single chambered	4.92 W/m^3	Pandit et al. [21]
3.	*Escherichia coli*	Lactic acid	Dual chambered	547 mW/m^2	Wang et al. [22]
4.	*Saccharomyces cerevisiae*	Glucose	Dual chambered	4.48 mW/m^2	Permana et al. [23]

Table 2 Mixed cultured bacteria as inoculum for MFC

Sl. No	Type of bacterial species	Substrate	Reactor design	Power density	References
1.	Activated sludge	Glucose	Dual chambered	560 mW/m^2	Martin et al. [24]
2.	Pretreated sludge	Glucose	Dual chambered	115.6 W/m^2	Gurung et al. [25]
3.	Domestic wastewater	Sucrose	Dual chambered	44.52 mW/m^3	Wei et al. [26]
4.	Granular anaerobic sludge	Acetate	Single chambered	408 $\pm$ 26 mW/m^2	Cheng et al. [27]

to complex combinations of organic matters. Till the last few decades, the main utilization of the MFC was carried out for wastewater treatment, where waste streams and activated sludge were used as the substrate. Today, the concept of waste to wealth and waste management including reuse and recycle has gained more emphasis due to which a large number of substrates were introduced in MFC [28]. Researchers focused on distinct basic characteristics of MFCs operating primarily with pure cultures such as glucose, acetate, lactate, and glycerol. In most of the literature, acetate has been the best choice of the pure culture substrate due to its simpler nature and high carbon source for the degradation by the microorganisms. Research demonstrated by [29] where the authors compared the performance of the MFC with various substrates including acetate, butyrate, propionate, and glucose. It was observed that the acetate-based substrate resulted in 72.3% of columbic efficiency which was highest among all the peers.

At the same time, complex carbon-rich organic matters such as municipal wastewater, dairy wastewater, and cassava mill wastewater are also being introduced. The use of solid waste as raw materials has been gaining popularity in recent years. Table 3 shows the performance of the MFC with various complex substrates.

The use of the liquid substrate is more prominent than the solid. This might be due to the simplicity with which wastewater can be handled, stored, and accessed at

Table 3 MFC performance with various complex substrates

Sl. No	Substrate	Reactor design	Volume	Power density (mW/m^2)	References
Liquid-based substrate					
1.	Domestic wastewater	Single chambered	28 mL	420	Choi et al. [30]
2.	Cassava mill wastewater	Dual chambered	30 L	1771	Kaewkannetra et al. [31]
3.	Palm oil mill wastewater	Dual chambered	450 mL	22	Baranitharan et al. [32]
4.	Human urine	Dual chambered	172 mL	23	Cid et al. [33]
5.	Chocolate industry wastewater	Dual chambered	800 mL	1600	Patil et al. [34]
6.	Swine wastewater	Single chambered	70 mL	2300	Ichihashi and Hirooka [35]
Solid-based substrate					
7.	Cowdung	Dual chambered	500	11.4	Sharma et al. [36]
8.	Rice bran	Single chambered	800	16.5	Yoshimura et al. [37]
9.	Human excreta	Single chambered	3000	142	Yazdi et al. [38]
10.	Kitchen waste	Single chambered	28	924	Adebule et al. [39]

the commercial and industrial levels [11]. The major challenge faced while using the solid substrate in MFC, in spite of higher energy density, is its low digestibility [37]. The presence of the higher complex bio-polymers like lignin makes the substrate necessary to be predated before the use in MFC [40].

The substrate concentration or COD too significantly affects the performance of MFC. The substrate concentration, which may be quantified in terms of COD, is directly related to the power generation in MFC. However, indeed, further increase after the optimum level results in inhibition of its own microorganisms and the output gets reduced drastically [41].

3.3 Electrode Material

Electrode material plays an indispensable role in the overall electrical performance as well as the cost of the MFC. It is certain that different electrode materials have different physical and chemical properties. A good anode/cathode material should possess the properties like higher electrical conductivity, surface area, stability, good

compatibility with the biocatalyst, high porosity, and most significantly non-corrosive nature [42]. Microbial adhesion, electron transport, electrode resistance, and kinetics of electrode surface responses are all affected by these properties [43]. Materials like Copper (Cu) although have higher conductivity as compared to others but it turned out to be unsuitable due to the high toxicity for the microorganisms and high corrosive properties [44].

In practice, the most commonly used electrode material includes carbon-based materials, metal and metal oxides, polymers, and composite materials. In the category of carbon-based materials carbon rods, forms, felts, cloth, brushes. graphite, graphite oxides, etc. are actively used. The research conducted by the authors [45] demonstrated that the utilization of carbon mesh electrodes and its pretreatment with ammonia gas led to excellent power generation (with a maximum power density of 922 mW/m^2) and reported carbon mesh as the most cost-effective material for the electrodes. Pretreatment of electrodes has become a major practice in order to obtain a proper surface and removal of contamination and to increase atomic N/C ratio.

The metals and metal oxides are too felicitated as the electrode material, but there remain some challenges [44]. Materials like stainless steel are extremely non-corrosive, but they fail to achieve high power due to smooth surface which does not allow the adhesion of bacteria over the electrodes. Also, metals like gold, silver, and platinum show excellent performance but the cost becomes a significant barrier [46].

The recent advancement in electrode material includes the use of graphene derived from natural biomass and waste material. [47] investigated the use of waste material to manufacture green reduced graphene (rGO) composite for anodes in MFCs to get more successful outcomes in regards to power generation and wastewater treatment. This resulted in the overall power density of 33.7 W/m^3 at a current density of 69.4 A/m^3 with a 75% shorter start-up time period. A very few literature can be found with waste material derived graphene-based material for electrodes, and thus need further attention. The reusability of waste biomass materials is a viable approach for increasing MFC efficiency without incurring large cost.

3.4 Membrane

A dual-chambered MFC constitutes a cation/proton exchange membrane (CEM) which separates the anodic and cathodic chambers. The main objective of a membrane is to pass the protons and does not allow the movement of the substrate from anodic to cathodic chamber or the diffusion of oxygen from the cathodic to the anodic chamber [9]. In practice, two kinds of membranes are commonly used: non-porous/dense membranes and porous membranes [48] and can be identified by their morphological characteristics as shown in Fig. 3.

Nafion-based membranes are the most commonly used membranes in the field of MFC due to high ionic conductivity and proton permeability [50]. The diffusion coefficient of the cations in the Nafion membrane is much higher than the others and thus have gained more popularity [49]. The cost of Nafion is comparatively

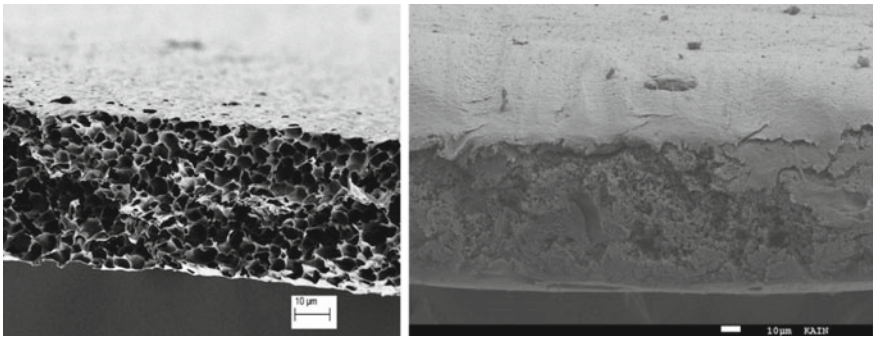

Fig. 3 SEM image of porous and non-porous membranes [49]

higher thus, low-cost agar and NaCl-based salt bridges are also being used in MFC applications [51]. A threefold increase in the power density was observed by the use of Nafion 117 as compared to the NaCl-based salt bridge of the same size with *Enterobacter cloacae* bacterial strain [52]. Moreover, the pretreatment of the Nafion membrane produced two times more power than the untreated membrane. In the same investigation, biofouling has been found to be a negative effect on membrane performance [53]. An economic analysis between Nafion 117 and sulfonated poly ether ether ketone (SPEEK) carried out by the researchers found MFC with SPEEK as PEM has a higher power per cost than that of the MFC with Nafion 117. This leads to the conclusion that the SPEEK system is more (almost two times) more cost-effective than Nafion [48]. Thus, it is very much essential to wisely choose membrane material looking into its cost as well as other performance affecting parameters.

3.5 Operating Condition

Researchers carried out various investigations on MFC in different operating conditions. This includes pH, temperature, mode of operation (batch/ continuous), ionic strength, etc. [54]. Higher wastewater acidity or alkalinity has an impact on both the effectiveness of wastewater treatment and the environment inside the reactor. To conserve microorganisms and support biological treatment processes, the pH of wastewater should be kept around neutral. But in the case of most of the wastewater, the pH is found to be lower which affects the overall performance. It was obtained that a better performance (Power density of 12.5 mW/m^2 & COD removal efficiency of 96.5%) was obtained at pH of 8.0 while using rice mill wastewater inside an earthen pot reactor [55].

Moreover, the neutral pH condition leads to a low concentration of proton transfer and high internal resistance in MFC. The solution conductivity can be improved by raising the ionic strength to lower the internal resistance without affecting the solution pH level. The addition of high saline substances helps to increase the kinetics of

the proton transfer from the anodic chamber to the cathodic chamber. The results suggested that the system's overall performance was improved by adding up to 20 g L^{-1} of NaCl, which reduced internal resistance by 33% and increased maximum power generation by 30% [56].

Temperature too has a very high impact on the MFC performance. It plays an important role in the rate of oxidation reaction, bacterial growth and sustainability, the kinetics of proton transfer through the medium, etc. [57]. As it is well known that the anodic chamber of MFC is seal-tight and at the anaerobic condition for the degradation of the substrate by the bacteria. Hence, the optimum temperature for the anaerobic digestion has to be considered in the case of MFC. The most probable temperature is at the room temperature or slightly higher (20–35 °C) [15]. The major challenges experienced during the low-temperature operation are the longer start-up time and lower current generation. In fact, it is quite difficult to generate electricity at a temperature below 15 °C even after months of operation. It was investigated that with an increase in temperature by 7 °C results in a 24% increase in power density [58]. At the same time with further increase till 55°C no steady power was obtained. Thus, MFC has to be operated at a particular optimum temperature in order to get maximum output.

3.6 Losses in MFC

Every system exhibits certain losses during the conversion process from one form to the other. The performance of MFC is too restricted by certain unavoidable losses which result in lower voltage and current outputs. The maximum theoretical voltage that may be achieved in a single fuel cell is 1.1 V, however, in practice, this voltage is substantially lower. Although these losses cannot be completely eradicated, but certainly their effect can be minimized using certain techniques and optimizations (Fig. 4).

The losses involved with a typical MFC system are indicated by the voltage equation given below.

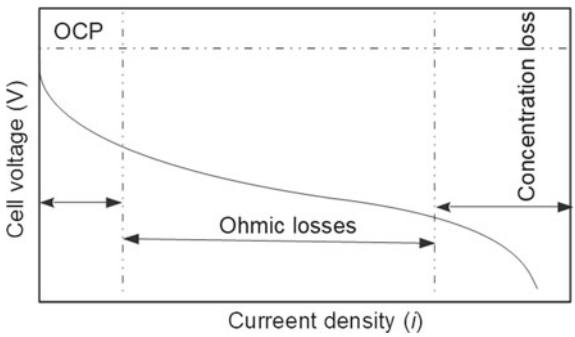

Fig. 4 Polarization curve of a typical MFC showing different losses

$$E_{\text{cell}} = E_{\text{emf}} - \left(|\sum \eta_a| + |\sum \eta_c| \right) + IR \tag{3}$$

where

E_{cell}	total output EMF
E_{emf}	EMF generated by the MFC
IR	sum of all Ohmic resistance
$\lvert \sum \eta_a \rvert$	anodic over-potential
$\lvert \sum \eta_c \rvert$	cathodic over-potential.

The major limiting factors that are most significant in MFC technology have been identified as ohmic losses, activation losses, concentration or mass transfer losses. The V-I curve or the polarization curve acts as a tool to study the performance and various losses occurring in the MFC.

3.7 Ohmic Losses

The main attributes of this type of losses are due to the resistance offered by the various interconnections to the movement of the electrons through the outer circuit as well as the flow of the proton through separating membrane [7]. The internal resistance offered by the MFC can degrade the performance to an excessive extent if not restricted. This comprises anode, cathode, and connecting wire resistance, electrolyte resistance, and membrane resistance (if any) [59]. The ohmic losses, in terms of voltage, can be combined as electronic as well as ionic loss as shown in Eq. (4)

$$V_{\text{ohmic}} = iR_{\text{ohmic}} = i(R_{\text{elec}} + R_{\text{ionic}}) \tag{4}$$

These losses can be minimized by loading of high conductive materials (platinum or gold) as electrodes, minimizing the space between the cathode and anode, using a low-resistive membrane, increasing the surface area of the electrodes and CEM, increasing the ionic strength of the electrolyte to a maximum tolerable level by the microorganisms.

4 Activation Losses

For carrying out any oxidation, or reduction reaction, activation energy is needed. In MFC the oxidation of substrates or reduction at bacterial surface demands a certain amount of activation energy that might result in a loss of energy and is referred to as activation losses [60]. As a result of which activation losses are always associated with any chemical conversion system. This loss is observed during the transfer of the electrons to the electrode surface in MFC. Tafel equation (Eq. 5) helps to compute the activation losses [61]. The equation establishes a relation between overvoltage at the electrode surface and the natural logarithm of the current density.

$$\Delta V_{\text{act}} = -A\ln(i) \tag{5}$$

where

ΔV_{act} Activation Loss (Voltage)
A Slope of Tafel Line
i Current Density.

The activation loss decreases with the increase in the current density and vice versa. Increases in electrode surface, operating temperature, electrode catalysis, and the formation of an enhanced biofilm on the electrode can all help to alleviate this problem [62].

4.1 Concentration Losses

Concentration losses occur when the substrate in the anodic chamber is oxidized faster than the produced electron is transferred to the electrode (anode) surface. Due to the restricted mass transfer of chemical species to the electrode through diffusion, it happens most commonly at high current densities [63]. This raises the ratio of oxidized to reduced species at the electrode surface and may lead to a rise in the anodic potential. This might be attributed to the anode's enhanced oxidative strength in MFC which hinders the maximum attainable MFC voltage.

Mass transfer losses can be reduced by distributing oxidants such as atmospheric air over the cathode compartment. Furthermore, optimizing MFC operating parameters, electrode material, and cathode compartment design may lead to lesser losses and better performance [64].

5 Future Perspectives of MFC

The MFC holds various challenging aspects in its further development and commercialization and it is high time to discuss the matter (Fig. 5). There is a wide range of scope of improvement in its performance for the deployment of it in various industrial as well as automobile applications [65]. The losses which are caused by the unwanted chemical reactions including the metabolic reactions of the microorganisms and oxidation of the raw material by oxygen diffusion should definitely be addressed [66]. The major application of MFC which is coming up for large-scale projects is wastewater treatment. The fundamental goal of the MFC scale-up is to increase the energy production per unit volume of wastewater. This is achievable only with the increase in the overall wastewater handling capacity, higher organic concentration of the wastewater or by stacking the MFCs in hybrid series-parallel connections [67]. But it is found that with high organic concentrations of the wastewater, (which results in higher electrical performance) the Chemical Oxygen Demand (COD) removal is typically decreased. As a result of which a series of the hydraulic stack of MFC has to be used in order to meet the demands of complete wastewater treatment plants [68]. The COD removal investigated by [69] was found to be around 200 mg/L/day which is very lower as compared to other waste-to-energy technologies like anaerobic digestion (25,000 mg/L/day). At the same time, a higher power density attainable system has to be designed since the MFC lacks to generate notable electrical output. There could be various reasons including the high internal resistance and other forms of losses which needs to be tacked down. Thus, it is necessary to incorporate significant changes in the overall MFC system.

Today a major emphasis is given on optimizations of reactor components and operating conditions. The materials used mainly in the electrodes and membranes should have a longer lifetime and lower cost, for the MFC technology to be competitive with other alternative renewable waste-to-energy systems. The use of the various

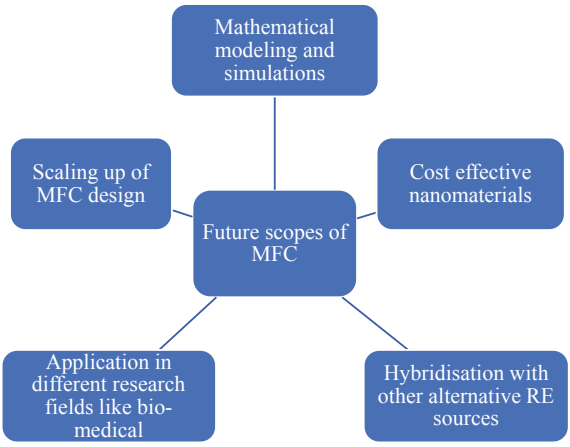

Fig. 5 Future scopes for successful application of MFC

nano-composite materials has a lot of potential for electrode modifications which helps in higher mass transfer to and from the electrodes. Various transition metal oxides (Tungsten oxide, Nickel oxide, Cerium oxide, etc.) are now being in major focus as an alternative of the platinum for use in reduction reactions [70]. Moreover, improved electron transport methods between the electrode and the biocatalyst are still being worked on. Research suggested the use of smaller granular carbon anode acts as an excellent material for the current production. The rough surface structure and porosity of the electrode enable microorganisms to trap the oxygen that helps in respiration [71].

MFC's cost is one of the major challenges which is yet to be overcome. Although low-cost laboratory-scaled designs are already being reported by various researchers, but in the case of large-scale application it has become a major cause of concern. A research conducted in Virginia Polytechnic Institute and State University, Blacksburg, USA, by designing a 200 L MFC system for wastewater treatment with 60% of its total project cost only utilized in the membrane material. The overall capital cost for that system was calculated to be $58 per gallon per day of the treatment capacity [72]. Low-cost membrane material with the characteristics like high proton conductivity, environment-friendly, easy availability, high stability, longer operational life, antifouling properties, etc. is the need of the hour for better performance [73]. The recent trends in the use of bionics and nanotechnology can be observed in membrane synthesis. In fact, membrane-less MFC alternatives can also be utilized in order to avoid the problem of the fouling of the membrane which improves the electrical output [74]. Mathematical modeling is another important aspect that has to be looked upon for the further development of the MFC. This helps in critically combining our understanding of the MFC, its processes involved, identifying the controlling elements in power production, and providing guidance for scale-up methods [75]. The up-gradation of the MFC could only be possible by simulating and validating the laboratory-based results. In order to control the simulation results, specific modeling tools and a working environment with a deeper grasp of multidisciplinary systems with boundary conditions must be designed and developed [76]. The MFC is now not only being focused on wastewater treatment and electricity generation from the bio-waste. The technology has gained interest in a wider scope of science and engineering. Researchers have tried to find its implacability in the field of biomedical science [77], marine science [78] space technology [13] electronic and communication engineering [79], etc. Various in-situ biosensors can be further developed with this technology to monitor the various contaminants like heavy metals, radionuclides, chlorinated solvents, etc. from the wastewater [80].

Although it is challenging for this technology to compete with the other existing alternative sources in terms of energy generation. At the same time, there remains a way of hybridizing it with the systems like anaerobic digester which utilizes the same substrate as MFC. Research carried out by [81] using landfill leachate as the raw material, mentioned that hybridization led to enhance cost-effectiveness, high biogas yield, and better performance in terms of electricity generation without the use of external mediators and expensive catalysts.

6 Conclusion

The concept of generating electricity in biological fuel cells exists in theory, but it is a relatively recent way of energy generation in practice. MFC technology refers to an innovative method of employing microorganisms to generate bioelectricity by oxidizing organic raw materials ranging from synthetic pure substrates like acetate or glucose to a complex combination of organic substrates such as domestic wastewater, industrial carbon-rich waste material, cow dung, and kitchen waste. Although MFC is a revolutionary method of producing bioelectricity from renewable resources, it faces certain challenges which hinder its large-scale implementation and commercialization. The judicious use of the materials for various MFCs components is very much important in order to increase the performance as well as to bring down the cost. Recent advances in material science, along with nanotechnology, may give one-of-a-kind tools for producing, transporting, and using electrical energy captured from MFCs. In spite of all the challenges, MFC holds a greater potential to compete with the existing renewable energy sources. Progression in the evolution of MFC technology may be accomplished thorough research of these elements and their optimal ranges that increases its performance.

References

1. IEA (2021) I.E.A. Electricity market report. https://www.iea.org/reports/electricity-market-report-july-2021. Accessed 30 Nov 21
2. Pimentel D et al (2009) Food versus biofuels: environmental and economic costs. Hum Ecol 37(1):1–12
3. Javed MS et al (2020) Solar and wind power generation systems with pumped hydro storage: review and future perspectives. Renew Energy 148:176–192
4. Steele BC, Heinzel A (2011) Materials for fuel-cell technologies. Materials for sustainable energy: a collection of peer-reviewed research and review articles from nature publishing group. World Scientific, pp 224–231
5. Bhargavi G, Venu V, Renganathan S (2018) Microbial fuel cells: recent developments in design and materials. In: IOP conference series: materials science and engineering. IOP Publishing
6. Lovley DR (2006) Microbial fuel cells: novel microbial physiologies and engineering approaches. Curr Opin Biotechnol 17(3):327–332
7. Logan BE et al (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40(17):5181–5192
8. Potter MC (1911) Electrical effects accompanying the decomposition of organic compounds. Proc R Soc London. Ser B Contain Pap Biol Charact 84(571):260–276
9. Logan BE (2008) Microbial fuel cells. Wiley
10. Balat M (2009) Microbial fuel cells as an alternative energy option. Energy Sour Part A: Recov Utiliz Environ Effects 32(1):26–35
11. Sarma R, Tamuly A, Kakati BK (2021) Recent developments in electricity generation by microbial fuel cell using different substrates. Mater Today: Proc
12. Chaudhuri SK, Lovley DR (2003) Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat Biotechnol 21(10):1229–1232
13. Tharali AD, Sain N, Osborne WJ (2016) Microbial fuel cells in bioelectricity production. Front Life sci 9(4):252–266

14. Reardon PN, Mueller KT (2013) Structure of the type IV a major pilin from the electrically conductive bacterial nanowires of Geobacter sulfurreducens. J Biol Chem 288(41):29260–29266
15. Aghababaie M et al (2015) Effective factors on the performance of microbial fuel cells in wastewater treatment—A review. Environ Technol Rev 4(1):71–89
16. Oh S, Logan BE (2005) Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Res 39(19):4673–4682
17. Sammes N (2006) Fuel cell technology: reaching towards commercialization. Springer Science & Business Media
18. Mathuriya AS (2013) Inoculum selection to enhance performance of a microbial fuel cell for electricity generation during wastewater treatment. Environ Technol 34(13–14):1957–1964
19. Sharma V, Kundu P (2010) Biocatalysts in microbial fuel cells. Enzyme Microb Technol 47(5):179–188
20. Ishii SI et al (2008) Comparison of electrode reduction activities of Geobacter sulfurreducens and an enriched consortium in an air-cathode microbial fuel cell. Appl Environ Microbiol 74(23):7348–7355
21. Pandit S et al (2014) Improvement of power generation using Shewanella putrefaciens mediated bioanode in a single chambered microbial fuel cell: effect of different anodic operating conditions. Biores Technol 166:451–457
22. Wang C-T, Chen W-J, Huang R-Y (2010) Influence of growth curve phase on electricity performance of microbial fuel cell by Escherichia coli. Int J Hydrog Energy 35(13):7217–7223
23. Permana D et al (2015) Preliminary investigation of electricity production using dual chamber microbial fuel cell (dcMFC) with Saccharomyces cerevisiae as biocatalyst and methylene blue as an electron mediator. Procedia Chem 17:36–43
24. Martin E et al (2010) The influence of operational conditions on the performance of a microbial fuel cell seeded with mesophilic anaerobic sludge. Biochem Eng J 51(3):132–139
25. Gurung A et al (2012) Effects of substrate concentrations on performance of serially connected microbial fuel cells (MFCs) operated in a continuous mode. Biotech Lett 34(10):1833–1839
26. Wei L et al (2012) Study on electricity-generation characteristic of two-chambered microbial fuel cell in continuous flow mode. Int J Hydrog Energy 37(1):1067–1073
27. Cheng K et al (2017) Aerobic granular sludge inoculated microbial fuel cells for enhanced epoxy reactive diluent wastewater treatment. Biores Technol 229:126–133
28. Pant D et al (2010) A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Biores Technol 101(6):1533–1543
29. Chae K-J et al (2009) Effect of different substrates on the performance, bacterial diversity, and bacterial viability in microbial fuel cells. Biores Technol 100(14):3518–3525
30. Choi J, Ahn Y (2013) Continuous electricity generation in stacked air cathode microbial fuel cell treating domestic wastewater. J Environ Manag 130:146–152
31. Kaewkannetra P, Chiwes W, Chiu T (2011) Treatment of cassava mill wastewater and production of electricity through microbial fuel cell technology. Fuel 90(8):2746–2750
32. Baranitharan E et al (2015) Effect of biofilm formation on the performance of microbial fuel cell for the treatment of palm oil mill effluent. Bioprocess Biosyst Eng 38(1):15–24
33. Cid CA et al (2018) Urine microbial fuel cells in a semi-controlled environment for onsite urine pre-treatment and electricity production. J Power Sour 400:441–448
34. Patil SA et al (2009) Electricity generation using chocolate industry wastewater and its treatment in activated sludge based microbial fuel cell and analysis of developed microbial community in the anode chamber. Biores Technol 100(21):5132–5139
35. Ichihashi O, Hirooka K (2012) Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. Biores Technol 114:303–307
36. Sharma I et al (2015) Bioelectrogenesis detection of inoculums using electrochromic tungsten oxide and performance evaluation in microbial fuel cells. J Electrochem Soc 163(3):F183
37. Yoshimura Y et al (2018) Electricity generation from rice bran by a microbial fuel cell and the influence of hydrodynamic cavitation pretreatment. ACS Omega 3(11):15267–15271

38. Yazdi H, Alzate-Gaviria L, Ren ZJ (2015) Pluggable microbial fuel cell stacks for septic wastewater treatment and electricity production. Bioresour Technol 180:258–263
39. Adebule A, Aderiye B, Adebayo A (2018) Improving bioelectricity generation of microbial fuel cell (MFC) with mediators using kitchen waste as substrate. Ann Appl Microbiol Biotechnol J 2(1):1008
40. Zhao Q et al (2017) Microbial fuel cell with high content solid wastes as substrates: a review. Front Environ Sci Eng 11(2):13
41. Chandrasekhar K, Mohan SV (2012) Bio-electrochemical remediation of real field petroleum sludge as an electron donor with simultaneous power generation facilitates biotransformation of PAH: effect of substrate concentration. Biores Technol 110:517–525
42. Cheng S, Liu H, Logan BE (2006) Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. Environ Sci Technol 40(1):364–369
43. Zhou M et al (2011) An overview of electrode materials in microbial fuel cells. J Power Sour 196(10):4427–4435
44. Yaqoob AA et al (2020) Recent advances in anodes for microbial fuel cells: an overview. Materials 13(9):2078
45. Wang X et al (2009) Use of carbon mesh anodes and the effect of different pretreatment methods on power production in microbial fuel cells. Environ Sci Technol 43(17):6870–6874
46. Pu L et al (2014) Silver electrodeposition on the activated carbon air cathode for performance improvement in microbial fuel cells. J Power Sour 268:476–481
47. Cheng Y et al (2018) In situ fabrication of green reduced graphene-based biocompatible anode for efficient energy recycle. Chemosphere 193:618–624
48. Mayahi A et al (2013) Effect of operating temperature on the behavior of promising SPEEK/cSMM electrolyte membrane for DMFCs. Sep Purif Technol 106:72–81
49. Rahimnejad M et al (2014) A review on the effect of proton exchange membranes in microbial fuel cells. Biofuel Research J 1(1):7–15
50. Du Z, Li H, Gu T (2007) A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. Biotechnol Adv 25(5):464–482
51. Kumar S, Kumar HD, Gireesh Babu K (2012) A study on the electricity generation from the cow dung using microbial fuel cell. J Biochem Technol 3(4)
52. Mohan Y, Das D (2009) Effect of ionic strength, cation exchanger and inoculum age on the performance of microbial fuel cells. Int J Hydrog Energy 34(17):7542–7546
53. Ghasemi M et al (2013) Effect of pre-treatment and biofouling of proton exchange membrane on microbial fuel cell performance. Int J Hydrog Energy 38(13):5480–5484
54. Rodrigo M et al (2007) Production of electricity from the treatment of urban waste water using a microbial fuel cell. J Power Sour 169(1):198–204
55. Behera M et al (2010) Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH. Bioelectrochemistry 79(2):228–233
56. Lefebvre O et al (2012) Effect of increasing anodic NaCl concentration on microbial fuel cell performance. Biores Technol 112:336–340
57. Liu H, Cheng S, Logan BE (2005) Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. Environ Sci Technol 39(14):5488–5493
58. Li L et al (2013) Effect of temperature change on power generation of microbial fuel cell. Environ Technol 34(13–14):1929–1934
59. Fan Y, Sharbrough E, Liu H (2008) Quantification of the internal resistance distribution of microbial fuel cells. Environ Sci Technol 42(21):8101–8107
60. Goud RK, Mohan SV (2011) Pre-fermentation of waste as a strategy to enhance the performance of single chambered microbial fuel cell (MFC). Int J Hydrog Energy 36(21):13753–13762
61. Boccaletti C et al (2006) Simulation models of fuel cell systems. In: Proceedings of the ICEM, electrical machines, p 6
62. Singh D et al (2010) Microbial fuel cells: a green technology for power generation. Ann Biol Res 1(3):128–138

63. Koroglu EO et al (2019) Scale-up and commercialization issues of the MFCs: challenges and implications. Microbial electrochemical technology. Elsevier, pp 565–583
64. Rismani-Yazdi H et al (2008) Cathodic limitations in microbial fuel cells: an overview. J Power Sour 180(2):683–694
65. Karmakar S, Kundu K, Kundu S (2010) Design and development of microbial fuel cells. Curr Res Technol Educ Top Appl Microbiol Microb Biotechnol, 1029–1034
66. Chandrasekhar K et al (2018) Challenges in microbial fuel cell and future scope. Microbial fuel cell. Springer, pp 483–499
67. Pandit S, Savla N, Jung SP (2020) Recent advancements in scaling up microbial fuel cells. Integrated microbial fuel cells for wastewater treatment. Elsevier, pp 349–368
68. Janicek A, Fan Y, Liu H (2014) Design of microbial fuel cells for practical application: a review and analysis of scale-up studies. Biofuels 5(1):79–92
69. Zhang X et al (2015) COD removal characteristics in air-cathode microbial fuel cells. Biores Technol 176:23–31
70. Mustakeem M (2015) Electrode materials for microbial fuel cells: nanomaterial approach
71. Arends JB et al (2012) Suitability of granular carbon as an anode material for sediment microbial fuel cells. J Soils Sediments 12(7):1197–1206
72. Ge Z, He Z (2016) Long-term performance of a 200 liter modularized microbial fuel cell system treating municipal wastewater: treatment, energy, and cost. Environ Sci: Water Res Technol 2(2):274–281
73. Palanisamy G et al (2019) A comprehensive review on microbial fuel cell technologies: processes, utilization, and advanced developments in electrodes and membranes. J Clean Prod 221:598–621
74. Xu J et al (2012) Fouling of proton exchange membrane (PEM) deteriorates the performance of microbial fuel cell. Water Res 46(6):1817–1824
75. Oh ST (2010) Trend of mathematical models in microbial fuel cell for environmental energy refinery from waste/water. In: EKC 2009 proceedings of the EU-Korea conference on science and technology. Springer
76. Jadhav DA et al (2021) Modeling and optimization strategies towards performance enhancement of microbial fuel cells. Biores Technol 320:124256
77. Bettin C (2006) Applicability and feasibility of incorporating microbial fuel cell technology into implantable biomedical devices. The Ohio State University
78. Dumas C et al (2007) Marine microbial fuel cell: use of stainless steel electrodes as anode and cathode materials. Electrochim Acta 53(2):468–473
79. Thomas YR et al (2013) A single sediment-microbial fuel cell powering a wireless telecommunication system. J Power Sour 241:703–708
80. Tront JM et al (2008) Microbial fuel cell biosensor for in situ assessment of microbial activity. Biosens Bioelectron 24(4):586–590
81. Mansoorian HJ et al (2020) Evaluating the performance of coupled MFC-MEC with graphite felt/MWCNTs polyscale electrode in landfill leachate treatment, and bioelectricity and biogas production. J Environ Health Sci Eng 18(2):1067–1082