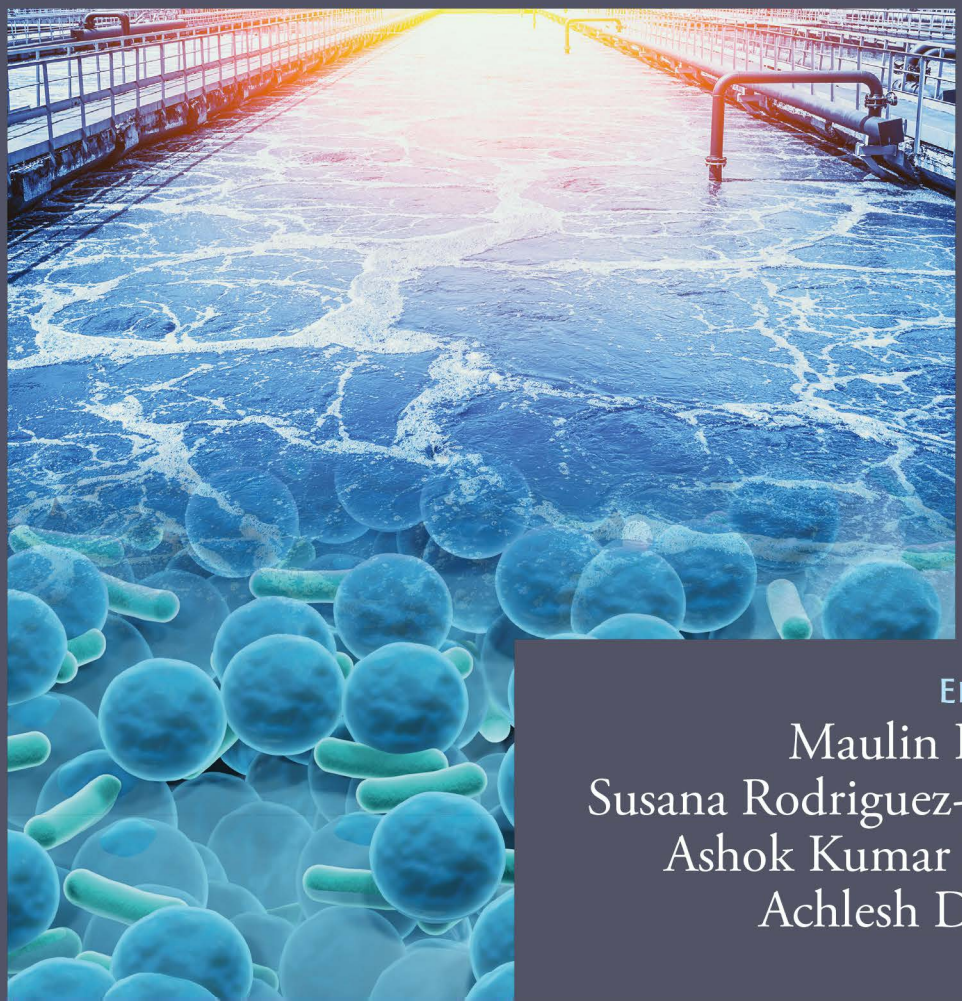
Development in Wastewater Treatment Research and Processes

# Bioelectrochemical Systems for Wastewater Management



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# Development in Wastewater Treatment Research and Processes

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# Contents

Contributors ..... xiii

**CHAPTER 1 Microalgal mediated bioelectricity generation and concomitant value-added products recovery from wastewater treatment in the bioelectrochemical system: Current status and future perspectives..... 1**
*Prathap Somu and Subhankar Paul*

**1.** Introduction ..... 1
1.1 Algae-based MFC ..... 2
1.2 The role of algae in MFCs ..... 4
1.3 Operational parameters of A-MFC influencing bioelectricity generation ..... 4
1.4 Algae MFC reactor ..... 6
1.5 Algal biofilm bioreactors ..... 8
**2.** Microbial carbon capture cell ..... 9
**3.** Value-added products recovery from algae-based MFCs ..... 10
**4.** Current status and future perspectives ..... 11
**5.** Conclusion ..... 11
References ..... 11

**CHAPTER 2 Algal microbial fuel cell: An innovative and accessible approach..... 17**
*Komal Agrawal and Pradeep Verma*

**1.** Introduction ..... 17
**2.** Construction of algal microbial fuel cells ..... 18
2.1 Electricity generation using algae at the cathode or anode ..... 18
**3.** Role of various parameters in algal microbial fuel cells ..... 20
3.1 Temperature ..... 21
3.2 pH ..... 21
3.3 Substrate ..... 21
3.4 Electrodes and membrane ..... 22
3.5 Light intensity ..... 22
3.6 Carbon dioxide and dissolved oxygen ..... 22
**4.** End-product in APMFC ..... 23
**5.** Limitations and prospects ..... 24



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6. Conclusion ..... 24
Conflict of interest ..... 25
References ..... 25

**CHAPTER 3 Key role of microorganisms in industrial wastewater treatment ..... 31**
*Nahid Siddiqui and Praveen Dahiya*

1. Introduction ..... 31
2. Sources of water pollution ..... 33
3. Diversity of microbes in wastewater ..... 37
   3.1 Bacteria ..... 37
   3.2 Protozoa ..... 37
   3.3 Algae ..... 38
   3.4 Fungi ..... 38
   3.5 Virus and helminths ..... 39
4. Role of microorganisms in industrial wastewater treatment ..... 39
   4.1 Paper and pulp industry ..... 39
   4.2 Textile industry ..... 40
   4.3 Food and beverage industry ..... 41
   4.4 Pharmaceutical industry ..... 42
5. Conclusion ..... 43
   References ..... 43

**CHAPTER 4 Membrane-integrated BES for wastewater reclamation ..... 49**
*Vandana Gupta*

1. Introduction ..... 49
2. Bioelectrochemical system (BES) ..... 50
3. Membrane-integrated BES (MIBES) ..... 51
   3.1 Types of membranes for BES ..... 51
   3.2 Classification of membrane-integrated BES ..... 53
   3.3 Challenges associated with MIBES ..... 58
   3.4 Advantages and disadvantages ..... 59
   3.5 Future perspectives and conclusion ..... 59
   References ..... 59

**CHAPTER 5 Wastewater remediation for reuse through emerging technologies ..... 61**
*Mir Sahidul Ali, Jonathan Tersur Orasugh, Suprakash Sinha Ray, and Dipankar Chattopadhyay*

1. Introduction ..... 61

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**2.** Advance technologies for wastewater remediation ..... 62
2.1 Advanced oxidation processes (AOPs) ..... 62
2.2 Adsorption ..... 63
2.3 Ozonation ..... 64
2.4 Membrane filtration technologies (MFTs) ..... 65
2.5 Biological wastewater treatment technology ..... 69
2.6 Desalination technology ..... 70
2.7 Nanotechnologies for heavy metals and metalloids remediation in contaminated water ..... 70
**3.** Wastewater treatment for water security in the water-energy Nexus for developing countries ..... 73
**4.** Conclusion ..... 73
Acknowledgments ..... 74
References ..... 74

**CHAPTER 6 Bioelectrochemical systems: Understanding the basics and overcoming the challenges ..... 79**
*Neha Tavker and Nakul Kumar*

**1.** Introduction ..... 79
**2.** BES and its classification ..... 80
2.1 Principle and thermodynamics of BES ..... 81
2.2 Microbial ES ..... 82
2.3 Enzymatic ES ..... 83
**3.** Necessity and working of BES ..... 84
**4.** Types of electron transfer in BES ..... 85
4.1 Extracellular ..... 85
4.2 Intracellular ..... 86
**5.** Applications of BES ..... 87
5.1 Recovery of nutrients ..... 87
5.2 Valorizing carbon dioxide ..... 87
5.3 Valorizing contaminated water ..... 88
5.4 Valorizing energy ..... 88
5.5 Product formation and recovery ..... 89
5.6 Recalcitrant pollutant degradation ..... 90
**6.** Factors affecting BES ..... 91
6.1 Effect of type of electrode ..... 91
6.2 Effect of different substrate ..... 91
6.3 Effect of reactor type ..... 92
6.4 Effect of pH ..... 92
6.5 Effect of temperature ..... 92
6.6 Effect of external resistance ..... 93

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7. Shortcomings of BES ..... 93
8. Conclusion and future prospects ..... 94
References ..... 94

**CHAPTER 7 Emerging trends of cyanobacteria-based microbial fuel cells as an alternative energy source ..... 99**
*K.P.A. Imanthi, D.A.T. Madusanka, M.M. Pathmalal, and F.S. Idroos*

1. Introduction ..... 99
   1.1 World energy crisis ..... 99
   1.2 Most common alternative energies ..... 99
2. Microbial fuel cell (MFC) as an alternative energy source ..... 102
   2.1 The basic structure of the MFC ..... 103
   2.2 Components of MFC system ..... 104
   2.3 Advantages of MFC over other alternative energy sources ..... 106
3. Water pollution and waste management ..... 106
   3.1 Different MFC systems for wastewater and leachate treatment ..... 107
4. Challenges associate with MFC ..... 109
   4.1 Activation losses ..... 110
   4.2 Ohmic losses ..... 110
   4.3 Concentration losses ..... 111
5. Advantages of cyanobacteria-based MFC over other MFC systems ..... 111
6. Future perspectives of MFC ..... 113
7. Conclusion ..... 114
   References ..... 115

**CHAPTER 8 Bioelectrochemical systems: Basic concepts and types ..... 121**
*Moupriya Nag, Dibyajit Lahiri, Sougata Ghosh, Dipro Mukherjee, Ankita Dey, and Rina Rani Ray*

1. Introduction ..... 121
2. Mechanism of working of BES ..... 122
   2.1 Anodic mechanism ..... 122
   2.2 Cathodic mechanism ..... 123
3. Types of BES ..... 124
   3.1 Microbial electrochemical system ..... 124
   3.2 Enzyme-mediated electrochemical system ..... 126

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4. Transfer of electron in bioelectrochemical system ....126
4.1 Extracellular transfer of electrons .... 126
4.2 Extracellular transfer of electrons .... 126
4.3 Interspecies transfer of electrons.... 127
4.4 Intracellular transfer of electrons .... 128
5. Applications in wastewater treatment....128
5.1 High and low biodegradable component of wastewater.... 128
5.2 Integrated processes for the treatment of wastewater..... 129
6. Conclusion and future prospects....129
References.... 129

**CHAPTER 9 Anode modification: An approach to improve power generation in microbial fuel cells (MFCs)..... 133**
*Gini Rani, Vijay Jaswal, and K.N. Yogalakshmi*

1. Introduction ....133
2. Microbial fuel cell....134
3. Electrodes and its properties....135
4. Anode modification in MFC....137
4.1 Carbon anode and its modifications.... 138
4.2 Pt anode in MFC .... 143
4.3 Nickel anode and its modifications in MFC.... 143
4.4 Conductive polymer for anode modification in MFC.... 144
4.5 Chemical anodic modifiers in MFC.... 145
4.6 Anode modification using metal oxide nanocomposites.... 146
5. Conclusion....147
References.... 147

**CHAPTER 10 Influence of operational parameters on the performance of microbial fuel cells ..... 153**
*Sanchita Bipin Patwardhan, Rujul Deolikar, Moupriya Nag, Dibyajit Lahiri, Dipak A. Jadhav, Rina Rani Ray, and Soumya Pandit*

1. Introduction ....153
2. Physical parameters influencing the performance of MFCs....154
2.1 MFC reactor components .... 154
3. Biological factors influencing the performance of MFCs....166

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3.1 Type of inoculum ..... 166
3.2 Substrate in anodic chamber ..... 171
3.3 Methanogenesis in microbial fuel cells..... 175
3.4 Start-up time for the operation of the MFC..... 176
**4.** Chemical and operational factors influencing the performance of MFCs .....176
4.1 Substrate type ..... 176
4.2 External resistance..... 176
4.3 Organic loading rate (OLR) ..... 177
4.4 pH..... 177
4.5 Temperature..... 178
4.6 Ionic strength and conductivity..... 178
**5.** Future prospects .....179
**6.** Conclusions .....179
References..... 179

**CHAPTER 11 Development of bioelectrochemical systems integrated nanocomposite membranes for wastewater management..... 191**
*Vishnu Manirethan, Neethu Shajan, Alona Sara Sajan, Uddandarao Priyanka, and Arindam Sinharoy*

**1.** Introduction.....191
**2.** Types of membranes.....192
2.1 Polymer-based membranes..... 192
2.2 Ceramic-based membranes..... 193
2.3 Bio-based membranes..... 194
**3.** Impregnation of nanomaterials onto membranes.....194
3.1 Metal nanomaterials impregnated membranes ..... 194
3.2 Semiconductor nanoparticles impregnated membranes ..... 195
3.3 Melanin nanoparticles impregnated membranes..... 196
**4.** Hybrid BESs integrated with membrane-based technologies .....201
4.1 Microbial desalination cells ..... 201
4.2 Osmotic microbial fuel cells ..... 202
4.3 Microbial reverse-electro dialysis cells..... 203
4.4 Pressurized filtration-microbial fuel cells..... 204
**5.** Energy consumption and recovery.....207
**6.** Current challenges and future perspectives.....209
**7.** Conclusion.....211
References..... 211

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**CHAPTER 12 Industrial wastewater treatment using bioelectrochemical systems and the potential for energy recovery..... 219**
*Manoj Kumar, Arindam Sinharoy, Uddandarao Priyanka, and Khwairakpam Sanayaima Singh*

**1.** Introduction .....219
**2.** Configuration and operational mechanism of microbial electrochemical systems .....221
**3.** Wastewater treatment using bioelectrochemical systems .....227
3.1 Domestic or municipal wastewater treatment..... 229
3.2 Brewery/distillery wastewater treatment..... 229
3.3 Agricultural wastewater treatment ..... 230
3.4 Animal farming wastewater treatment ..... 230
3.5 Landfill leachate treatment..... 231
3.6 Palm mill oil effluent treatment ..... 231
3.7 Paper and pulp industry wastewater treatment ..... 232
3.8 Petroleum wastewater treatment ..... 232
3.9 Pharmaceutical wastewater treatment ..... 232
**4.** Conclusion and future perspectives.....233
References..... 233

**CHAPTER 13 Microbes and wastewater treatment..... 239**
*Vasant Kumar, Rutika Sehgal, and Reena Gupta*

**1.** Introduction .....239
**2.** Microbial diversity in the treatment of wastewater .....240
2.1 Role of bacteria ..... 241
2.2 Role of protozoa ..... 241
2.3 Role of metazoa..... 242
2.4 Role of algae..... 243
2.5 Role of fungi..... 243
**3.** Characteristics of wastewater .....244
**4.** Methodologies used for wastewater treatment.....245
4.1 Primary treatment ..... 246
4.2 Secondary treatment ..... 246
4.3 Tertiary treatment ..... 247
**5.** Role of 16S rRNA in the classification of microbes .....247
**6.** rDNA technology for wastewater treatment .....248
6.1 Elevating the rates of biodegradation using rDNA technology..... 249

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7. Technology for microbial electrical remediation....250
8. Conclusion....251
Acknowledgments....251
Conflict of interest....251
References....252

**CHAPTER 14 Challenges in the scale-up of MES for wastewater treatment....257**
*Jonathan Tersur Orasugh, Baba Gabi, Aisha Zaman, Priya Banerjee, and Dipankar Chattopadhyay*

1. Introduction....257
2. MES: Anode tuning for efficient electron generation....259
3. MES cathodes for utilization of $CO_2$ as a source for diverse chemical manufacture....262
4. Use of chemolithoautotrophs MES biocathodes for $CO_2$ reduction....264
5. $CO_2$ usage to make a variety of products using the MES systems....265
6. MES energy consumption reduction via integration of renewable energy and a chain-elongation platform....266
7. Future perspectives....269
8. Conclusion....271
Declaration of competing interest....271
Acknowledgments....272
References....272

Index....277

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CHAPTER

# 1 Microalgal mediated bioelectricity generation and concomitant value-added products recovery from wastewater treatment in the bioelectrochemical system: Current status and future perspectives

**Prathap Somu and Subhankar Paul**

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## 1. Introduction

Global warming and climate change have become major problems globally due to the extensive emission of carbon dioxide by various types of anthropogenic activities, including the burning of fossil fuels and deforestation [1]. Hence, there is a need for technologies that can sequester atmospheric carbon dioxide. The commonly used $CO_2$ sequestration methods are chemical physical adsorption and membrane separation techniques. However, these suffer greatly due to their very expensive nature as well as their involvement in the production of secondary toxic compounds, which thereby limits their application [2]. These limitations can be overcome by biological methods where $CO_2$ fixation can be efficiently carried out using bioelectrochemical systems such as photosynthetic microbes, cyanobacteria, and microalgae [3].

Bioelectrochemical systems can also be used for carbon sequestration along with the recovery of value-added products. The different types of bioelectrochemical systems (BES) are plant-microbial fuel cell (pMFC), microbial carbon capture cell (MCC), and microbial electrosynthesis (MES) [4]. The microbial fuel cell (MFC) is an evolving technology used in the treatment of wastewater for the production of bioelectricity and carbon sequestration. MFCs utilize organic substrates present



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in the wastewater, such as glucose, proteins, acetate, and other substrates, as a source of energy [5]. In the anode chamber of a microbial carbon capture cell, wastewater containing organic matter serves as a substrate for anaerobic microbiota called exoelectrogens, which degrade the organic compounds to protons, electrons, and $CO_2$ [6]; whereas the cathodic chamber contains photosynthetic microorganisms such as algae and cyanobacteria, which, in the presence of light illumination, produce biomass by converting atmospheric $CO_2$ or anode chamber $CO_2$ by releasing oxygen [7]. Another approach is microbial electrosynthesis (MES), which also produces organic compounds such as acetate by sequestering $CO_2$ with the help of biocatalysts.

The microalgae-based bioelectrochemical system is sustainable and promising due to the ability of microalgae to grow at a rapid rate and fix $CO_2$ with high efficiency through using organic compounds and nutrients from wastewater effluents. Microalgae are also grown in marginal land with lower amounts of water requirement and produce algal lipids for biodiesel production, carbohydrates for the production of bioethanol, and methane production by anaerobic digestion. The microalgae also produce an increased amount of biomass, which can be used as feedstock for cattle and fish. Microalgal biofuel production can also be coupled with wastewater treatment for cost-effective production of biofuel, as well as used to reduce the nutrients in aquatic systems, thus preventing eutrophication.

Recent studies have shown that the productivity of biomass with the efficiency of wastewater treatment has been reported to be improved by the application of algal biofilm reactors, where agricultural and domestic wastewaters are used as a substrate. Different types of biofilm reactors with support materials affect the production of biomass and the efficiency of wastewater treatment. This chapter gives insights into the application of the microalgae-based bioelectrochemical system for bioelectricity generation as well as biofuels value-added products using wastewater.

## 1.1 Algae-based MFC

Microalgae fuel cells are efficient compared to other MFCs due to the potential of microalgae to grow rapidly by extracting inorganic substances like nitrogen and phosphorus from effluents and atmospheric carbon dioxide to generate bioelectricity along with other valuable products that can be extracted from the microalgal biomass formed [8]. The microalgae are usually integrated into MFCs as microbial carbon capture cells or sediment MFCs, assisted cathode systems, and photosynthetic MFCs [9]. The interactions between the microalgae and the bacteria in a mixed culture have proved to be more efficient for the absorption of carbon dioxide, thus resulting in a reduced risk of emission of the carbon. The major advantage of algae-based MFCs (A-MFCs) is the production of oxygen by the microalgae in the light period, thus reducing the aeration cost, as the oxygen produced is utilized for the cathodic reactions [10].

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### 1.1.1 Photosynthetic algal microbial fuel cell

Photosynthetic algal microbial fuel cells (PAMFCs) are very similar to MFCs and are made up of either Plexiglas or another acrylic material for the easy absorption of light by the algal cells. The PAMFCs are usually either in a tubular, circular, cylindrical, rectangular, or H-shaped configuration, consisting of single, double, or three-chambered compartments [11]. In pilot-scale applications, the volume of the PAMFCs is about 200–1000 L. In PAMFCs the functioning of the MFC requires the electron acceptor $O_2$ produced by the microalgae that are available in the cathodic chamber of the MFC. Generally, the MFCs that are used to supply oxygen is small and comprise two similar 25–50 mL cubical or cylindrical compartments divided by a proton exchange or an ion-exchange membrane such as Nafion. PAMFCs are usually designed based on the cathode compartment's requirement of dissolved oxygen, such as the dissolved oxygen needed for the oxygen reduction reactions and as an acceptor of electrons [12]. Algae-based MFCs under suitable conditions produce power densities of about 153 $mW/m^2$, which is 32% more than the 116 $mW/m^2$ produced by mechanical aeration. The major disadvantage of these MFC is the high construction and operational cost associated with them.

### 1.1.2 Sediment microbial fuel cells (SMFC)

A sediment microbial fuel cell (SMFC) makes use of deposits made up of nanoparticles, such as carbon nanotubes, to improve the interaction between the electrolyte and the electrode, resulting in more effective electricity generation.

In algae-based sediment MFC, microalgae form the cathode and act as chamber electron acceptors. It has been documented that *Chlorella vulgaris* can be immobilized on carbon nanotubes that are used to supply oxygen to the aerophilic deposition mechanism at the cathode [13]. In a river SMFC, a rotating type of cathode was devised to balance the $O_2$ supply with an increased electricity production of 48 $mW/m^2$, in comparison with the 38 $mW/m^2$ produced by the algal SMFC. The algal SMFCs are primarily designed to boost the oxygen consumption rate [14]. The algal cathodes were made up of glass materials such as Plexiglas or another acrylic for the easy perforation of light through the cathodes consisting of carbon nanotubes made of graphite felt and coated with *C. vulgaris*. In a lab-scale experiment, with a maximal volume of 240 L, the oxygen reduction rate was increased by the usage of different types of graphite felt [15]. Under an ideal environment, algal-based sediment MFCs can generate electricity up to 21 $mW/m^2$, and the electricity produced rises to 38 $mW/m^2$ on the incorporation of multiwalled carbon nanotubes coated with *C. vulgaris* [16]. The decrease in $O_2$ provided by the biomass of algae supports a 2.4-fold increase in the electricity generated because of the integration of the nanotubes made of carbon in the cathodic chamber.

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## 1.2 The role of algae in MFCs

Cyanobacteria (blue-green algae) and microalgae play an important part as photosynthetic organisms on the planet Earth, in that they fix atmospheric carbon dioxide and thereby act as a prospective source for bioenergy conversion [17]. These photosynthetic microorganisms perform similar functions to that of bacteria during the production of electricity in MFCs [17].

Oxygen is a negatron that consumes the electrons released during the metabolic process in photosynthesis, thereby resulting in decrease in the volume of current produced [18]. The growth of the algal species, the content of chlorophyll, and the growth kinetics of the microalgae depend on the amount of sodium sulfate present in freshwater. The optimal concentration of sodium sulfate in the water changes the culture's ionic and osmotic characteristics, thus inducing many organic processes, and also has an advantageous outcome on the cell density. A higher concentration of sodium sulfate will have an inhibitory effect on algae growth and the chlorophyll content while providing the optimal concentration of sodium sulfate, reported to result in a positive outcome on algae growth and also help in maintaining the chlorophyll content required for photosynthesis [17]. To address this issue, and to reduce the oxygen synthesized by photosynthesis, sodium sulfite was introduced in the anodic region. In the power generation process, the microalgae are the electron donator, as was demonstrated by lowering $O_2$ concentration [19]. During the power generation process, the cell density and the magnitude of light reflected are proportionate to the photosynthesis process, which eventually increases the electricity produced by the MFC [20]. The conductivity, the optimum measurement, and the electrical resistance of the electrolyte are the main fundamental factors that can cause variations in power measurement.

## 1.3 Operational parameters of A-MFC influencing bioelectricity generation

Algal growth is influenced by the intensity of light encompassing the cathodic compartment, which in turn affects the production of oxygen, and thus, the complete outcome of the A-MFCs. The study performed on A-MFCs at various light and dark regimes, such as 18/6 h, 12/12 h, and 6/18 h, confirmed that lighting conditions have a powerful influence on the power generation of A-MFCs. In comparison to the A-MFCs operated under the other two conditions, higher time in the light—that is, in the 18/6 regime—produced a large amount of electricity [21]. The amount of dissolved oxygen was reduced to $0\,mg\,L^{-1}$ in the 6/18 light/dark regime, resulting in the A-MFC producing no power. It was found that when the light time was longer, such as 24/0 versus 16/8 h and 12/12 h, an A-MFC produced more power density. According to the above findings, algal photosynthesis occurs in the cathodic compartment and a greater power density has been achieved by using a longer light time. During the daytime, the algal biomass synthesizes more $O_2$ by carbon dioxide absorption, thereby maintaining the oxidation and reduction reactions (ORR),

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whereas the respiration process occurs at night time, leading to the consumption of oxygen and the depletion of DO concentration at the cathodic compartment, thereby lowering the overall efficacy of MFCs.

Experiments were carried out to study the effect of light intensity on the photosynthetic oxygen production in the cathode chamber and found the increase in light intensity resulted in the proportional increase in the DO concentration [8]. As the number of photons absorbed by the microalgae increases, the ionization rate of the chlorophyll also rises, resulting in higher NADPH and ATP accumulations in the algal cell; when the intensity of light was increased to 3500 from 1500 lx, for example, the dissolved oxygen concentration raised steadily to 13.2 mg $L^{-1}$ from 7.5 mg $L^{-1}$. The DO concentration in the catholyte has a big impact on the ORR at the cathode. Furthermore, the oxidation–reduction reactions of the cathode were inversely proportional to the DO concentration caused by the greater intensity of light, probably due to the mass transport limitation of the oxygen reduction on the cathode [22]. However, different species of algae have different optimum light intensities, such as 5000 lx for *C. vulgaris* and 7000 lx for the algal strains in mixed culture.

According to the Stefan-Boltzmann law, the environmental temperature is affected by the intensity of light. Although the temperature has little or no effect on light-dependent reactions like photosynthesis, it may either activate or deactivate the main enzymes in the photosynthetic process. The ideal condition for the microalgae, which was discovered to be between 20°C and 30°C, is required for a normal photosynthesis process catalyzed by light. When the water temperature in the cathodic chamber was raised to 31.2°C from 27°C, the DO concentrations also surged to 6.8 mg $L^{-1}$ from 3.7 mg $L^{-1}$, increasing from 3.7 to 6.8 mg $L^{-1}$ in an A-MFC with an open anode compartment. The application of various strains of algae in A-MFCs requires a range of optimal temperatures for growth and development as the temperature is an important parameter for the functioning of the A-MFCs, since temperature influences the microbial activity, enzyme and reaction kinetics, and mass transfer rate. However, it is reported that the selection of microalgae for A-MFCs from the area and geographical location of the test area will help in obtaining the optimal temperature in the required narrow range and result in better productivity.

For the increased biochemical reactions in A-MFCs, optimum temperatures of 30–35°C have been used in the majority of cases [23]. Moreover, scaling of A-MFCs in open areas requires plenty of sunshine, which is cost-effective with suitable precautions to prevent impairment to the A-MFC system as well as the environment. Most algal strains have optimal growth at a pH of 6.2–6.8, while very few algal strains show pH tolerance, although there is a stain that could survive even at pH levels around 9.5 with a slow growth rate. Furthermore, it was discovered that a slightly higher neutral pH in the cathode was optimum for effective ORRs in A-MFCs. The oxidation-reduction potential of the cathode (EORR) depends on the pH (EORR = 1.22–0.058 pH), so the output at pH 7 is 0.81 V, according to the Nernst equations. The most common cause of pH changes at the cathode is cation

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transfer to the cathode from the anode, which can disrupt the algal microecology in the cathode compartment. To prevent a sudden pH change in the cathodic region, different buffers, such as borax, carbonate, saline catholyte, phosphate, carbon dioxide, and zwitterionic buffers, were utilized. Carbonate and $CO_2$ appear to be more suitable in the context of A-MFCs because they are inorganic and can be easily exploited by the microalgae during the photosynthetic process and can ultimately produce $O_2$ [8].

The optimal $CO_2$ addition also has a major impact on A-MFC performance, as continuously sparing of $CO_2$ in the cathodic compartment for 0.5 h was reported to obtain sufficient for the growth of the algae [24]. Furthermore, increasing the carbon dioxide bubbling rate was found not to improve the A-MFC performance any further, implying that carbon fixation is limited [25]. The outcome of various carbon dioxide concentrations in $CO_2$-air mixtures (1%–7%, v/v) was studied in MCC and it was found that 5% of carbon dioxide-air mixture has the optimal amount for the highest generation of power. Overall, we can infer that determining the optimum $CO_2$ concentration needed for increased voltage and electricity production in an A-MFC is an important parameter and further study is required to obtain a clear understanding of the influence of these parameters individually, as well as the synergistic effect on A-MFC performance.

## 1.4 Algae MFC reactor

MFC research is ongoing and many new improved bioreactors have been designed to create low-cost facilities. Many MFC designs have been developed using a wide range of bacterial species, but only a few have attempted to use algal MFCs. A double compartmental cell was constructed with the help of a proton exchange membrane (PEM) separating the anodes from the cathodes. The sample was collected and the flow rates were maintained using a hollow cathode and anode where the circuits were connected using a peristaltic pump for operation. It is reported that nitrobenzene at the cathode had a significant impact on the electricity produced due to the interaction between the anode and nitrobenzene and that the presence of nitrobenzene altered the superior organisms on the anode [26].

PEM was used to separate a cubic-shaped MFC in which the utilized reference electrodes were made of Ag/AgCl. The graphite was used to produce the external current. The contamination on the electrode surface as well as trace metals were removed by the treatment with 1 M NaOH and 1 M HCL [27]. In this experiment, a catholyte, potassium ferricyanide ($C_6N_6FeK_3$), was used in a 100 mM potassium dihydrogen phosphate buffer after the pH was adjusted to 7 with 1 M NaOH. Various types of wastewaters were researched and assessed in this study to know the outcome of sewage sludge on various microbial communities. With ferricyanide, an A-MFC was developed that could operate in batch and continuous modes. A solution of glucose substrate (500 mL), wastewater (100 mL), vitamin mix, and minerals were present in the anode chamber (20 mL) [28]. The electrode was a

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carbon fabric that had been washed with 1 NaOH and 1 M HCL. To distinguish the anode and cathode, PEM was used as a membrane. This membrane was immersed in $H_2O_2$ for 1 h at 80°C, then in 0.5 M $H_2SO_4$ for 1.5 h at 80°C to remove impurities. In this system, the anode and cathode are linked using a copper wire and the voltage flowing across the circuit was measured using a digital voltmeter. Then an MFC was constructed with a dual-chamber unit. The compartments were separated by the cationic exchange membrane. The voltage of current passing through the circuit was measured using graphite electrodes having a platinum wire to provide the internal resistance. The wastewater was recycled continuously by a submersible pump where the water was pumped into the anodic chamber with $O_2$ being delivered to the cathodic chamber for the occurrence of the biochemical reactions.

A bottle-type MFC with dual chambers was constructed out of glass and utilized [29]. 5000 lm was set as the light source's brightness and silicone materials were used to completely seal the reactor openings. A dark environment was created by wrapping the whole reactor with aluminum foil for efficient electricity generation. Throughout the experiment, the cathode was made out of plain carbon paper. The researchers demonstrated that better results were produced by using a carbon fiber brush cathode (CFBC) rather than using a plain carbon paper cathode (PCPC). The current production increased due to the increase of the cathodic potential as a larger surface area was available in the CFBC electrode than in the PCPC electrode. Then, two Plexiglas culture vessels were utilized to construct a complicated MFC model reactor, one as an anode and the other as a cathode (tubular photobioreactor), where preacclimated bacteria were inoculated in the anode using glucose as a substrate. Fluorescent lamps, in a 12 h dark/12 h light cycle, were used as a light source for the cathode. A basic glass bottle MFC model reactor with a total 580 mL working volume and headspace of 30 mL was built. The top of the reactor consisted of two ports to measure the gas with the assistance of an $O_2$ sensor. Sodium bicarbonate ($2\,g\,L^{-1}$) was fed to the reactor as a carbon source and the dried algae served as the nitrogen source.

Before the experiment began, nitrogen (N2) gas was passed through both chambers to eliminate the oxygen present in the headspace. PVC was used to build three identical MFCs, each containing cathode and anode as two separate chambers [30]. The cathode in the above experiment was electrodes made by the cold-rolled gas diffusion process, and the anode was made of carbon cloth. The gas exchange between the cathode and the anode was prevented by ion-permeable separators, which were utilized to separate the cathode from the anode. Phosphate buffer solution (PBS) was used to pretreat all of the electrodes, and the reference electrodes used were the Ag/AgCl—3.5 M KCl. For the transfer of electrons through the circuit, the cathode and the anode were linked by a copper wire. These three MFCs were all run at room temperature. The dissolved $O_2$ (DO) was removed by flushing the $N_2$ gas continuously, and the setup was put on a magnetic stirrer to ensure that the liquid within the electrolytic cell was constantly stirred.

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## 1.5 Algal biofilm bioreactors

Algal biofilm bioreactors use different types of wastewater for biofuel production and also increase the production of biomass [31]. The nutrients are taken up in the cathode chamber by microalgae and biomass is formed, which is further used in the production of biohydrogen, bio-oil, biomethane, biodiesel, and bioethanol [8]. The primary wastewater treatment is done in the anode chamber of MFCs and the electricity is generated. The pretreated water containing carbon and other nutrients is utilized in the cathode chamber by the algal cells for metabolic functions and to increase the biomass concentration [32]. The microalgae also sequester $CO_2$ produced from the anaerobic digestion process and hence, minimize the discharge of gases into the atmosphere [33]. Different types of algal biofilm reactors, such as horizontal bioreactor, vertical bioreactor, flowcell bioreactor, rotating bioreactor, and rocker bioreactor, are used for wastewater treatment [31]. The rotating algal biofilm reactor is also used in the treatment of secondary effluent municipal wastewater with increased biomass productivity of $31\,g^{-2}d^{-1}$; the productivity of which was shown to be higher when compared with the suspended systems [34].

A higher biomass concentration of $96\,g\,L^{-1}$ was produced using the algae *Botryococcus braunii* in an algal biofilm photobioreactor. It is also shown that algal biofilm bioreactors are a cost-effective way of treating wastewater, along with higher biomass production with less energy consumption [35]. Gajda et al. produced a power output of 123 μW and increased biomass of $400\,mg\,L^{-1}$ with an algae bioreactor. The algal biomass can also be used as a substitute for the substrate as it has a high calorific value in biological processes [8]. There are different applications of biomass from algae in the production of lipids and other metabolites that are used in the pharmaceutical and cosmetic industries [36,69]. *C. vulgaris* is used in the production of pigments such as lutein, β-carotene, and chlorophyll, and also biomass from algae is used as feed for humans and fish, used for biogas production, and for other value-added products [8]. Biofilm supports effects on the biomass production of algae by increasing the surface area. We have summarized the various bioreactors used for algae culture in Table 1.1.

**Table 1.1** The bioreactor types used for the cultivation of algae and their corresponding biomass concentration.

| Reactor type | Algae | Biomass concentration | Ref |
|---|---|---|---|
| Horizontal biofilm reactor | *Botryococcus braunii* (LB572) | $0.71\,g^{-2}d^{-1}$ | [37,38] |
| | Microalgae consortium | $0.5–3.1\,g^{-2}d^{-1}$ | |
| Flow lane biofilm reactor | Mixed microalgae | $2.9\,g^{-2}d^{-1}$ | [39] |
| | *Scenedesmus obliquus* and *Chlorella vulgaris* | $5.5\,g^{-2}d^{-1}$ | [40] |

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**Table 1.1** The bioreactor types used for the cultivation of algae and their corresponding biomass concentration. —*cont'd*

| Reactor type | Algae | Biomass concentration | Ref |
|---|---|---|---|
| Vertical biofilm reactors (twin layer vertical reactor) | Mixture of *Chlorella vulgaris* strain SAG 211-11b, *Scenedesmus rubescens* | $6–12\,g^{-2}d^{-1}$ | [41,42,68] |
| Vertical biofilm reactors (multiple glass plates with algal disks) | M2630 and *Halochlorella rubescens* | $50–80\,g^{-2}d^{-1}$ | [43] |
| Rocker bioreactor | Chlorella | $2.57\,g^{-2}d^{-1}$ | [44] |
| | *Chlorella vulgaris* | $3.51\,g^{-2}d^{-1}$ | [45] |
| | *Chlorella sorokiniana* | $20\,g^{-2}d^{-1}$ | [46] |
| Rotating algal biofilm reactor | Mixed culture | $31\,g^{-2}d^{-1}$ | [47] |
| Photobioreactor (PBR) | *Botryococcus braunii* | $96\,gL^{-1}$ | [35] |
| Raceway pond | | $0.35\,gL^{-1}$ | |
| Flat photobioreactor | | $2.7\,gL^{-1}$ | |
| Tubular photobioreactor | | $1\,gL^{-1}$ | |

## 2. Microbial carbon capture cell

The microbial carbon capture cell (MCC) is a bioelectrochemical system where the algae present in the cathode perform carbon sequestration by feeding carbon dioxide generated by the anode for subsequent production of biomass and bioelectricity. The carbon dioxide is generated from anaerobic electrogenic microbes in the anode compartment by oxidative degradation of organic matter [48]. Microorganisms in the process of MCC help in higher $CO_2$ fixation for bioremediation from atmosphere or flue gases, increased microbial biomass production, production of value-added products, and high photosynthetic conversion efficiency [4]. $CO_2$ produced from fossil fuels such as coal, diesel, and petrol by the process of combustion and $CO_2$ from fermentation industries are used by MCC and, thereby, reduce the cost of $CO_2$ supply as well as reduce the emission of $CO_2$ from both microalgae and bacteria at the cathode and anode, respectively [49].

MCCs have an advantage over the PAMFCs in terms of low $CO_2$ emissions from the anaerobic chamber and also provide higher voltage outputs. MCCs can show increased power densities compared to that of MFCs by increasing the surface area at the cathode chamber and reducing the solution resistance [50]. A higher voltage of $630 \pm 30\,mV$ is produced in MCC with aeration than in MCC without aeration ($610 \pm 50\,mV$) [11]. MCCs are also affected by various factors such as physiological conditions such as pH of analyte and electrode for anodic chamber and

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$CO_2$ sequestration of growth of microorganisms in the cathodic chamber. They are also affected by other factors such as carbon source and light intensity, which is an important source of microbes for increased biomass production and the recovery of value-added products [51]. The wastewater from food and pharmaceutical industries and domestic and municipal wastewater can be treated by MCC and used for bioelectricity generation and production of value-added products [52].

## 3. Value-added products recovery from algae-based MFCs

The wastewater from food and pharmaceutical industries, and domestic and municipal wastewater can be treated by MCC and used in bioelectricity generation and production of value-added products [11]. Microalgae can simultaneously generate electricity as well as value-added products such as hydrocarbon fuels by hydrothermal liquefaction, biodiesel by Bligh and Dyer extraction or soxhlet extraction, biogas from algal anaerobic digestion with value-added chemicals such as lutein, β-carotene, zeaxanthin, chlorophyll, and canthaxanthin by hot or cold extraction or supercritical fluid extraction [53].

Value-added products can be synthesized from various species, which act as biocatalysts. It is reported that value-added chemicals can be recovered from both pure and mixed cultures [4]. The mixed cultures have more advantages over the pure culture in terms of implementation, feasibility, and maintenance of aseptic conditions [54]. The various microbial culture used in MFC and their synthesized value-added products are tabulated in Table 1.2.

**Table 1.2** Microbial culture and their value-added products synthesized used in MFC.

| S. no | Culture | Value-added products | Ref |
|---|---|---|---|
| 1 | *Sporomusa* | Biofuel | [55,56] |
| 2 | *Genetically modified Clostridium* | | |
| 3 | *Acetogens* | Acetate | [57] |
| 4 | *Methanogens* | | |
| 5 | *Thermophilic morella thermoautotrophica* | Acetate and formate | [58] |
| 6 | *Morella thermoacetica* | Acetate | [59] |
| | *Morella Thermoautotrophica* | | |
| 7 | *Geobacillus species strain* | Ethanol | [60] |
| 8 | *Geobacillus thermoglucosidasium* | | |
| 9 | *Megasphaera* sp. | Butyrate | [61] |
| 10 | *Homoacetogens* | Propionate | [62] |
| 11 | *Geobacter sulfurreducens* | Polyol | [63] |
| 12 | *Methanogens* | Methane and hydrogen | [4] |

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## 4. Current status and future perspectives

Microalgae in bioelectrosynthesis have been used in bioelectricity generation and recovery of value-added products with the treatment of wastewater effluents [64]. There are various challenges faced by microbial fuel cells, such as species selection, environment, and yield [65]. A few heterotrophic microalgal strains have been explored, but they facilitate large-scale microalgae culturing even under dark conditions and by using wastewater. The biomass and biofuels might be enhanced using genome editing technology such as CRISPR/CAS, ZFN, or TALEN to alter the genomic DNA of algal strains [66]. Microalgal biofuels have not been commercially produced, due to high operational cost, low biomass productivity, and high energy required [67]. The algal biomass is produced by suspended systems, namely, open and closed types. Closed types of bioreactors are expensive and, hence, not suited for the production of biofuels. The open-type systems have the problems of contamination and evaporation. The application of biofilm bioreactor in MFC overcomes the limitations accompanied with closed types of bioreactors and increases biomass production with less operational cost in the treatment of wastewater. However, scale-up experiments and validation for the integration of MFC and biofilm reactors using microalgae for treating wastewater and atmospheric $CO_2$ sequestration have to be evaluated before commercialization is possible in terms of economic feasibility.

## 5. Conclusion

Since microalgae can grow rapidly even in marginal land, the utilization of microalgae in MFC is ideal as a cost-effective way of treating wastewater and atmospheric $CO_2$ sequestration, which also facilitates bioelectricity generation and the recovery of value-added products, as compared to other MFC technologies such as P-MFC. However, microalgal-based MFC application is limited due to the high operating costs and high energy consumption in harvesting the biomass. Although multiple algal MFC bioreactors have been developed for wastewater treatment with simultaneous $CO_2$ sequestration, the field-scale demonstration of these MFC technologies is limited as a result of the varying yield and performance, which is affected by the operating parameters. Hence, it is important to consider operating parameters such as the selection of strains in both anode and cathode; to understand the biomass control, electron transfer, recovery, and scale-up; and the optimization of the modeling process for better productivity. Thus, a better synergy between the two technologies of MFC and biofilm reactor is required, for which streamlined research needs to be carried out to improve the economic feasibility for commercialization of the scale-up process.

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CHAPTER

# Algal microbial fuel cell: An innovative and accessible approach

2

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## 1. Introduction

The most prominent terminology currently used worldwide is bioenergy [1]. Energy production has been a major focus over a period of time, and numerous sources for the production of energy have been identified and explored, such as crops [2], non-food crops [3], and oil crops [4]. The major limitation of the various forms of crops being used for energy production is the requirement of huge land areas, which means these crops compete with agricultural land areas and areas where humans and animals live [5,6]. Thus, the search began for an alternative that required less space, less time to grow, and offered maximum energy production, e.g., microalgae [5,7]. Microalgae are an efficient alternative as they are a renewable, clean source and can reduce the dependency upon fossil fuel for energy production. In recent years, with the increase in energy demand, the use of microalgae for the conversion of solar energy into renewable bioenergy has played a crucial role and has garnered immense research interest from scientists globally [8].

The efficiency of utilization and conversion of solar energy by the higher plants varies from that in other photosynthetic organisms. In the cases of $C_3$ plants, $C_4$ plants, and algae, the conversion efficiency is 4.6%, 6%, and 9% respectively [9,10]. As in the case of plants, in algae, the initiation of photosynthesis is via photo induction in the cells of algae, resulting in the fixation of carbon for conversion to various storage compounds such as lipids, proteins, carbohydrates, etc. The algae have several advantages for use in biorefineries; however, their utility is restricted due to the cost associated with the conversion of algal biomass to value-added products. The harvesting itself constitutes 30% of the total production cost, making the process less economically viable [11]. Thus, various approaches are being devised for the efficient utilization and conversion of algal biomass. Of the various approaches, the microbial fuel cell has garnered attention, where the biocatalytic reaction of the microorganism catalyzes the organic substrate and converts it into electricity [12–16]. It is an uprising technology where cathode and anode chambers



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are separated by a proton exchange membrane [17]. Algae have been used in microbial fuel cells (MFCs), both in the cathode and the anode. At the cathode, algae are used to provide oxygen ($O_2$) and at the anode, algae are used as a substrate to support the growth of bacteria. Thus, the present chapter deals with the basic construction of algal photosynthetic microbial fuel cells (APMFCs), its role at cathode and anode. In addition, the effect of various parameters, the end-product formed in APMFC, challenges, and prospects are discussed.

## 2. Construction of algal microbial fuel cells

An MFC is used for the conversion of chemical energy to electrical energy. In the anodic chamber, carbon dioxide ($CO_2$) is produced by the oxidation of the organic feed; while in the cathodic chamber, an electron acceptor ($e^-$) e.g., $O_2$ or ferricyanide, accepts the excess proton from the anodic chamber and $e^-$ from the electrical circuit. Now, in the case of algal photosynthetic microbial fuel cells (APMFC), the algae convert $CO_2$ and light into biomass and $O_2$. In the study by Ali et al. [18], biomass derived from *Microcystis aeruginosa* was the $e^-$ donor in the MFC fed with microalgae, where the control was MFC fed with acetate. It was observed that the maximum power and current density of 83 $mW/m^2$ and 672 $mA/m^2$ was attained with MFC fed with microalgae along with complete removal of microcystin-LR and chemical oxygen demand (COD) removal efficiency of $67.5 \pm 1\%$ [18]. Sharma and Chhabra [19] reported the use of *Chlamydomonas reinhardtii* at the cathode in APMFC with power density, current density, specific growth rate, COD removal, and Columbic efficiency of 15.21 $W\,m^{-3}$, 39 $A\,m^{-}3$, 0.284 $day^{-1}$, 73.30%, and 9.068%, respectively. The total phenol, antioxidant activity, total chlorophyll, and total carotenoids were 157.69 mg GAE/g algae DW, IC50 = 67.07 μg/mL, 18.95 mg/g, 2.40 mg/g, and 2.40 mg/g, respectivelt. Thus, the efficiency of *Chlamydomonas reinhardtii* for both electricity generation and production of value-added products was reported (Fig. 2.1).

### 2.1 Electricity generation using algae at the cathode or anode

The role of algae in MFC at the cathode and anode is been discussed as follows.

#### 2.1.1 Cathode

The use of chemicals in cathodes generates pollutants and the use of air cathodes is expensive. Thus, the biocathode was developed, consisting of microorganisms where the electrochemical reduction is facilitated. Biocathodes are low cost, sustainable, and have less energy requirement. The use of algae in the MFC is the optimal way to reduce the consumption of energy. In the case of APMFC, first, the algae in the cathode release $O_2$ via photosynthesis and the biomass generated can be used for the generation of various value-added products [20–25] (Table 2.1).

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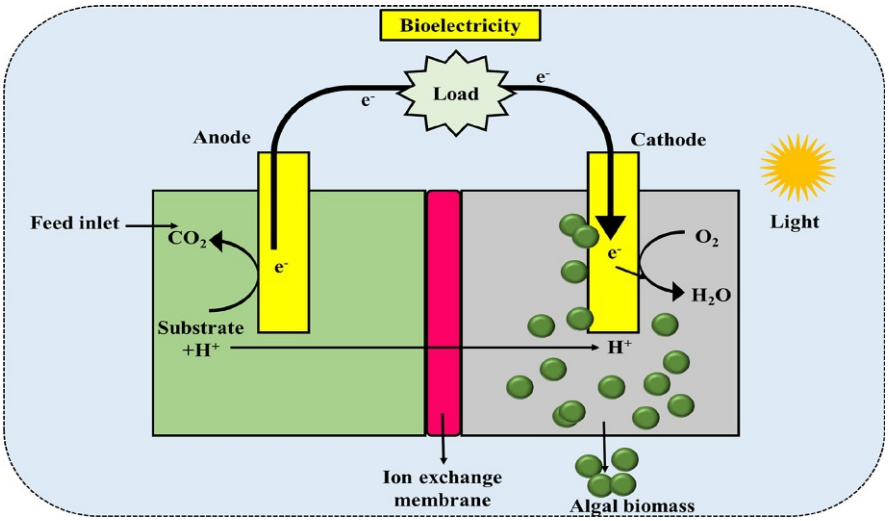


**FIG. 2.1**

Schematic representation of a basic algal photosynthetic microbial fuel cell (APMFC).

**Table 2.1** The APMFC at the cathode for electricity generation.

| Sl. no. | Algae at cathode | Feed at anode | Reference |
|---|---|---|---|
| 1. | *Chlorella vulgaris* | Activated sludge from a wastewater treatment plant in Spain | [19] |
| 2. | The top portion of the cathode was exposed to air and the bottom portion was exposed to kitchen waste anaerobically digested effluent | Anode was completely submerged in the wastewater | [26] |
| 3. | *Chlorella* sp. QB-102 | Activated sludge suspension | [27] |
| 4. | *Chlorella vulgaris* | Preacclimated bacteria (acclimated from domestic wastewater) | [28] |
| 5. | *Scenedesmus obliquus* | Wastewater from a plant in Korea | [29] |

### 2.1.2 Anode

The algae, when used at the anode as a substrate, focus primarily on wastewater treatment, whereas the bacteria in the wastewater act as the inoculum and thus, for generation of electricity. The various forms of algae, i.e., algae powder, live cells [30], and algae as the sole carbon source or $e^-$ have been reported [31]. It has also been suggested that extraction of $e^-$ from algae for electricity generation is a unique idea,

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**Table 2.2** The APMFC at the anode for electricity generation.

| Sl. no. | Algae at anode | Feed at cathode | Reference |
|---|---|---|---|
| 1. | Model 1: live microalgae<br>Model 2: live microalgae in both the anode and cathode<br>The strain used: *Chlorella pyrenoidosa* | Model 1: *potassium ferricyanide* | [32] |
| 2. | Dead microalgae biomass (*Scenedesmus*) | *Chlorella vulgaris (C. vulgaris)* AG30007 UTEX 0000265 | [33] |
| 3. | Biomass of *Chlorella regularis* | Phosphate buffer solution (50 mM, pH: 7.2) with $K_3[Fe(CN)_6]$ (100 mM) | [31] |
| 4. | Single chamber membrane-free bioelectrochemical systems<br>Low-cost biochar derived from algal biomass was used as anode material<br>*S. oneidensis* MR-1 with lactate | – | [34] |
| 5. | Single-chamber biophotovoltaic biofilms of *Chlorella* sp. coated in electrodes were used as the anode material | – | [35] |

however, for its effective implementation the $O_2$ levels should be negligible or maintained at minimum levels to regulate the process. This can be attained by purging $N_2$ or alternatively by adding high concentrations of salt [32]; although the latter is less preferred due to the consequent low current generation [9] (Table 2.2).

## 3. Role of various parameters in algal microbial fuel cells

The photosynthetic microorganism in the presence of solar energy converts organic compounds into electrical energy. It fixes $CO_2$ with the release of $O_2$, and light energy is converted into carbohydrates and other value-added compounds [36]. One of the major drawbacks of the system is that during photosynthesis $O_2$ is released and, as it is a strong $e^-$ acceptor, it has the potential to absorb $e^-$ generated during the metabolism, thus decreasing the current [37]. Therefore, to overcome the limitation, sodium sulfite was added to the anode to decrease the concentration of $O_2$ and, over time, the algae became the $e^-$ during the power generation [37,38]. It has also been stated that cell density and light intensity play crucial roles in the functioning of the APMFC. The other physiological factors that are involved in the enhancement of the APMFC are discussed as follows:

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## 3.1 Temperature

The high temperature enhances the reaction kinetics, reduces the internal resistance, and produces high mass transfer rate, increased growth rate, and accelerated biochemical reaction, along with increased current density and Columbic efficiency. While on the flip side, the high ionic conductivity decreases the Ohmic resistance [39]. Different temperatures have been suggested for the working of MFC; however, the optimum is suggested to be 35°C [9]. However, in the study by del Campo [40], the temperature maintained in a two-chambered MFC was $26 \pm 1$°C. Gajda et al. [41] reported the functioning of a fully biotic MFC in a 14-h light/10-h dark regime at 22°C. Thus, variations in the temperature range for the functioning of APMFC have been reported and may vary from strain to strain or the type of MFC used in the respective study.

## 3.2 pH

The pH at the anode usually lies between 6 and 8, and for the cathode is 7. The pH at the anode is critical for the proper functioning of the metabolic activities of the cells [12]. The variation in the pH of the APMFC results due to the change in the concentration of the $e^-$, protons, or $O_2$ thereby hampering the electricity generation of the system. The pH of the anode should be maintained at near-neutral pH with the maximum current generation and thus, effective steps should be taken, as any change severely hampers the thermodynamics and kinetics of the APMFC.

Furthermore, reduction of $O_2$ at the cathode results in alkaline pH [42]. The $O_2$ reduction potential can be calculated using the Nerst equation and, ideally, the cathode potential is 0.81 V at pH 7. However, the values vary in the case of experimental setup due to contamination by species/mixed potential effect/formation of hydrogen peroxide ($H_2O_2$) [9]. Furthermore, in the case of air cathode or single-chambered MFC, the pH (8–10) of the system, rather than affecting them individually, affects both the cathode and the anode. The high pH also inhibits the growth of the bacterial community in the anodic chamber, although it favors that of the cathodic compartment. This parameter thus enhances the functioning of the MFC [43]. In addition, the cathodic efficiency can be enhanced by the addition of economically feasible catalysts [44], buffers [45–49], salt [50], carbonate [51], and zwitterion [52].

## 3.3 Substrate

A variety of substrates have been used as a feed for APMFCs, such as kitchen wastewater [53], swine wastewater [54], industrial fruit juice wastewater [55], landfill leachate wastewater [56], dye wastewater [57], etc. The rate of substrate degradation is directly proportional to the power density [58]. Furthermore, to enhance the efficiency of the system, the substrates/feed can be pretreated for better hydrolysis, e.g., by heat [59], solid-liquid separation [60], etc. It, however, has to be considered that,

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although this increases/enhances the system output, it is an energy-intensive process and thus at a commercial level can be a limitation.

## 3.4 Electrodes and membrane

The other factors that affect the functioning of the APMFC are the electrodes and membrane. They play a critical role in the functioning of the APMFC, and including them in the design while simultaneously being economically viable is a major challenge [61]. In the case of electrodes, extensive study with respect to the material has been carried out that has a high surface area, high conductivity, low resistance, is cheap, and has enhanced stability [9]. Similarly, in the case of the membrane, the material used directly affects the transfer rate of the chemical species involved in the reaction, which ultimately has either a positive or negative impact on the functioning of the APMFC [17].

## 3.5 Light intensity

In the case of the algae cathode MFC, both reduction and oxidation occur when a 12 h light and dark cycle is provided. In the light phase (oxidation), $O_2$ and biomass are produced, and in the dark phase (reduction), consumption of $O_2$ and oxidation of organic matter occurs. In the study by Wu et al. [62] with optimum light and dark cycles, the production of power can be increased with a decrease in cathodic resistance. On the other hand, in the case of Juang et al. [63], two ranges of light were applied, i.e., 6–12 and 12–18 W. The production of power was higher at lower light intensity. In addition, the difference in power generation of covered vs uncovered in the anode chamber was 4.41 mW/kg COD/day. Thus, the covered anodic chamber exhibited high voltage, power density, Coulombic efficiency, and specific power as compared to the uncovered anodic chamber. Therefore, it can be stated that the optimization of the intensity and duration of light also plays a crucial role in the functioning of APMFCs (Fig. 2.2).

## 3.6 Carbon dioxide and dissolved oxygen

Media components with a supply of $CO_2$ are required for the improved photosynthetic reaction. In the study by del Campo et al. [40], $CO_2$ sparging of 30 min in the cathode resulted in optimal growth, whereas Wang et al. [28] directed the $CO_2$ produced by bacteria from the anode chamber to the cathode. As $CO_2$, dissolved $O_2$ is a crucial parameter for the functioning of MFC [64]. The concentration of dissolved $O_2$ varies due to the light (high) dark (low) cycle and temperature. The variation in the temperature might be due to the surrounding ambiance and the change in light intensity to maintain the light-dark cycle, where the increase in light intensity from 6 to 26W increased both photosynthesis and concentration of dissolved $O_2$ [63]. The three parameters, i.e., temperature, dissolved $O_2$, and photosynthesis are

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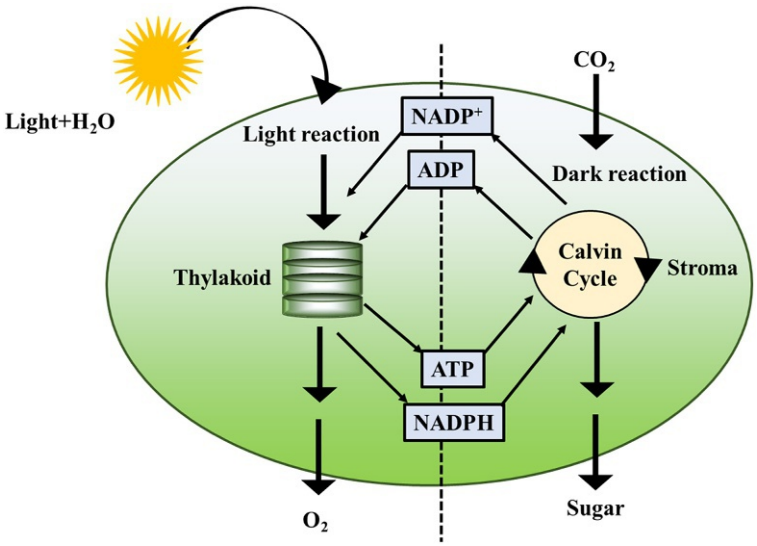


**FIG. 2.2**

Schematic representation of the light and dark reaction in algae.

interdependent of each other. As the light intensity (3500 lx) increases, the dissolved $O_2$ and photosynthesis increase [62]. However, with further increase in light, the production of power decreases, which is regarded as photo-inhibition [28].

## 4. End-product in APMFC

The algal biomass obtained from an APMFC can be used for the generation of various value-added products, such as biodiesel, biogas, and biohydrogen, providing tremendous potential in the biorefinery industry. In the case of biodiesel production, direct transesterification of wet algal biomass omitting the extraction step renders the process economically feasible. This one-step process enhances the process efficiency and reduces waste [26,65–67,83] . In the case of bioethanol, as the microalgae cells lack lignin, unlike plants, they do not require a pretreatment step before the fermentation. Although treatment to release the carbohydrate from the cell is required, it is also preferred to used de-oiled algal biomass if the pretreatment step has to be skipped. The most common fermentation microbe used is *S. cerevisiae* (activity lowers at high salt concentration), and thus, it is advisable to use salt-tolerant *S. cerevisiae* [68]. The other strain that has been reported for fermentation is *Zymomonas mobilis* [69,84]. In the case of biohydrogen, the most common strains reported are *Scenedesmus obliquus* and *Chlamydomonas reinhardtii* [70] in the presence of hydrogenase (majorly involved in biohydrogen production) and currently, genetic

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engineering-based studies are being used to increase its yield further for future use [71,72]. Lastly in the case of biogas, organic compounds are digested under aerobic conditions by a specific group of microbes to produce $CO_2$ and methane [73,74].

## 5. Limitations and prospects

The APMFC is sustainable, nonhazardous, renewable, and thus has gained the interest of countries globally. It is at the forefront of research to provide tremendous renewable resources to the human race with ecosystem sustainability. The major limitation, however, is its implementation at a commercial scale for the end-product to be available commercially. Additional research with the integration of an interdisciplinary approach including genetic engineering has to be undertaken for is successful commercialization. Furthermore, the application of algae has extended its application in various sectors, such as pharmaceutical [75], biomedical [76], nanotechnology [77], beauty [78], health [79], food [80], bioremediation [81], etc. The other major limitation of APMFC is the requirement of a large surface area for the light to be received at the cathode chamber, followed by harvesting of biomass and extraction of value-added products, which would increase the cost so much that its upscale would not be feasible.

In the case of $CO_2$ sequestration by algae, an autotrophic mode of cultivation is preferred, which is limited in the presence of light. On the contrary, in the light phase, if the biomass load increased tremendously, the light penetration is restricted, thus limiting the growth of algae. Therefore, a chamber with a larger surface area and better light penetration is required [37,82]. In the case of the anode, the Columbic efficiency and utilization of substrate along with performance stability of the identical start-up protocol are low. It has to be noted that for the functioning of APMFC the consumption and the production have to balance for the optimal working of the system. The research and development sector should focus on enhancing the power output with efficient use of biomass for conversion to various value-added products or extend its application in biorefineries. Research into the installation of full-scale APMFC should be initiated to make the entire process a reality and of service to mankind.

## 6. Conclusion

The APMFC has tremendous potential in its future application in various sectors, and globally, scientists (Fig. 2.3) are developing technologies and methodologies to make it a reality. Global research has increased exponentially over the past few decades. Furthermore, with technological advancement, the research associated with microalgae has widened its application over a diverse spectrum. Microalgae are fascinating and hold great future opportunities for researchers with the potential to impact the entirety of the human living system.

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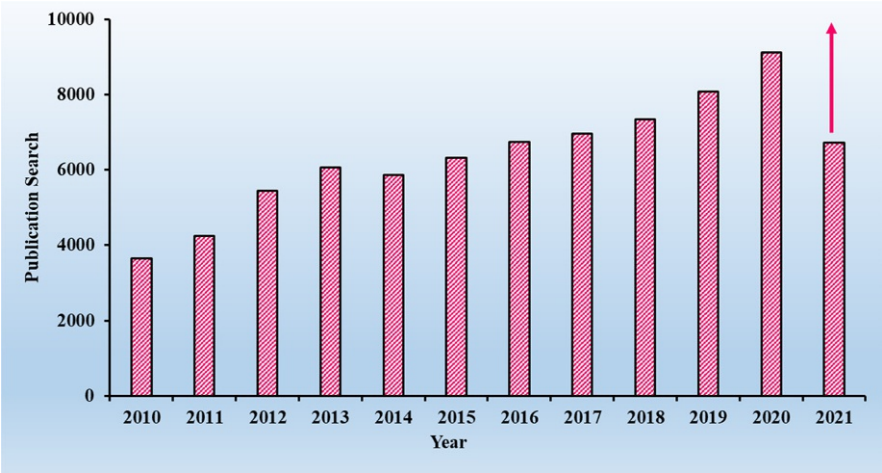


**FIG. 2.3**

The year-wise increase in the publication of algal photosynthetic microbial fuel cell (APMFC) research in google scholar (https://scholar.google.com/).

## Conflict of interest

The authors declare no conflict of interest.

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CHAPTER

# Key role of microorganisms in industrial wastewater treatment

3

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## 1. Introduction

Anthropogenic effects have caused huge stress on the global environment. Despite the fact that humans have made their lives more comfortable and leisurely, and also since the world economic growth has shown a steep rise in the past few decades, the thoughtless industrial growth has caused abundant harm to the ecosystems and environment at large. With recurrence of economic and social activities, the problem of environmental pollution is widespread, and industrial pollution is posing several challenges [1]. Industries release effluents containing dangerous organic and inorganic pollutants, which pollute the rivers, lakes, streams, and adjoining soil environment affecting life [2]. Increasing water pollution poses grave threat to human population and is proving hazardous not only for human health but also for sustained development and economy. The influence of these pollutants on living organisms proves harmful on account of the direct or chronic toxicity of these substances or their degradation by-products. Large parts of the world's population cannot exercise one of the basic rights of access to clean drinking water. If the problems of water pollution are left unchecked, its inexorable effect of human health will increase. Reserving and using funds for the amelioration of sanitation infrastructure is the urgency of the present times. Worldwide reports of subsurface water contamination with heavy metal have become an earnest public health concern, and with respect to this, information of the wastewater source is of prime importance, and it is crucial to identify its biological, chemical, and physical facets and to conduct a suitable treatment strategy [3].

With better research facilities, several technologies for water treatment have been developed and are being improved upon. As per the classification of the wastewater source concerned, the treatment technologies may be divided into chemical, biological, and physical treatment techniques. These can also be classified as in situ technologies, those used for remediation at site and ex situ, wherein the pollutants are removed at a remote place [4]. Coagulation and flocculation are excellent examples of in situ treatment of groundwater and surface water, using chemical treatment.



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A physical method called water diversion is used for diversion. These methods, however, may be less popular as flocculation uses chemicals and if used in in large amounts could be hazardous for the user and water diversion is not all cost effective if used on a large scale [5].

Treatment of wastewater using the biological method or technology is perhaps the best treatment technology for wastewater. This technology also called as biodegradation involves the breakdown or degradation of organic compounds by bacteria, fungi, and other microorganism producing carbon dioxide and water or methane [6]. The role of microbes has been vastly exploited since centuries, for several products like enzymes, biofuels, and probiotics. These microorganisms, on an industrial scale, also play a key role in the degradations of pollutants and thus help in maintaining the balance in the ecosystem by cleaning up the toxic wastes. In contrast to other treatment methods, biological wastewater treatment is relatively cost effective, gives very less secondary excretion of pollutants, and has lesser damaging effects on the environment [7].

Water is used in a lot of ways, affecting the quality and the quantity of available water. The regulation of resources and pollution of water have important roles to play at national and international levels. The water in the streams, lakes, rivers, reservoirs etc. is the surface water and is usually needed for irrigation purposes and drinking besides being used to cool the electricity generating equipment in thermoelectric plants. When rainwater seeps deep into the earth, filling the cracks, crevices, and porous spaces in what is known as saturated zone, it becomes groundwater—one of our least visible but most important natural resources. The top surface's saturated zone is called the water table. The pressure of the water below the water table permits the water to enter the wells, from where water can be drawn out for human consumption. The formation of rock above the water table (aquifers) through which the rain percolates to replenish the water table is called as the zone of aeration or the unsaturated zone. Ground water and surface water are interconnected. Surface water is hydraulically connected to ground water. Surface water transudes into the ground and becomes ground water while as the ground water resurfaces and replenishes the surface. The exchange occurring between the surface water and groundwater continues when rivers emerge from mountains and flow across the state's large valleys. Winter flooding, along with rainfall in the valleys, recharges groundwater during the winter. Some of that groundwater moves back into rivers and helps maintain flow in the dry season. Shallow groundwater also supports wetlands and vegetation on the banks of streams, lakes, etc. (riparian zones). Water movement between the two water systems can lead to mixing of their qualities. Ground water has less contamination since rocks work as filter to remove wastes, but nutrients and other chemicals present in surface water can diffuse into the ground water, thereby contaminating it. Aquifers that become contaminated will discharge into streams can lead to long-term contamination of surface water; streams can contaminate aquifers also. Ground water can be a potentially long term and one of the major contributors of surface water contamination.

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## 2. Sources of water pollution

Polluting agents produced by the ruthless planning done by humans has contaminated our water bodies. These pollutants can be classified as point source and nonpoint source. Pollution that emerges from a single, identifiable, and isolated source is called point source pollution. These can easily be identified and managed. Important point sources are industrial premises, towns, agricultural installations, manure storage, and landfills. The pollutants are discharged into the environment directly from sources where these can be gauged. Releases from isolated sources identified as "point source pollution." Point source coming from mining, smelting, refining, and other industry have polluted harbors and industrial areas worldwide, giving rise to some of the most acute incidents of trace metal toxicity in natural waters [8]. Nonpoint pollution does not come from a specific source or point, instead, it originates from many places, or from a widespread area. Pollutants from nonpoint sources move into the environment by complex pathways. As water moves through the ground or over a land, and, on the way, picks up natural or man-made pollutants, adds this into different natural water bodies or underground water is a nonpoint pollution. The agricultural, industrial, and urban runoffs are major contributors of nonpoint pollution [9]. Transboundary pollution enters the environment at one place and shows its impacts at places that are hundreds and thousands of miles away. Radioactive waste is one such example, which travels enters the oceans through the nuclear reprocessing plants and shows its effects in countries far away.

In addition to the above division of contaminating sources, two types of contamination of water are observed. (1) Emergency contamination that occurs due to a catastrophic impact causing death of the fauna and flora inhabiting the water bodies, in addition to other harmful effects. (2) Long-term contamination is evident by persisting organic pollution. It poses a negative effect on the environment within the water bodies causing nonappearance of some species of fish in the associated zones of river, as it affects the food chains of the organisms inhabiting these water bodies. Wide range of pollutants exists in the environment depending on the sources from where they emerge.

1. Nutrients such as nitrogen and phosphorus are often associated with fertilizers, animal wastes and plant debris. These are found in the agricultural and residential run offs. Municipal wastewater also contains nitrogen and phosphorus even if it has received conventional treatment. Unwanted nutrients not only inhibit the growth of aquatic plants but also kill fish in the affected water bodies. Both N and P enrichment happens because of the use of agricultural and urban use of land around the water sheds. Phosphorus gets carried in storm run offs after it gets attached to inorganic sediments. Also, phosphorus is predominantly present in industrial discharges, domestic effluents, and in agricultural fertilizers. Nitrogen fertilizer is the main source of N in water bodies [10]. From the soil nitrogen leaches and enters the groundwater, it may also move with organic matter. Cultural eutrophication is caused due to high concentration of N and P

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resulting in increased growth of aquatic algae. Prolific growth of these algae, called as algal blooms, is harmful as form a thick mat of algae very close to the surface, blocking sunlight and clogging fish gills, thus damaging the water ecosystem. Aquatic systems show nutrient enrichment due to human activities from point and nonpoint sources. Point sources of nutrients are relatively easy to monitor and control as compared to nonpoint sources from agricultural fertilizers, livestock, and urban runoff, which manifest both temporal and spatial variability. Nonpoint sources of nutrient enrichment are a major source of water pollution worldwide [11]. Nitrogen and sulfur are codifying compounds and cause acidification of inland water that proves harmful for the ecosystem and affects the fish.

2. Oxygen demanding substances such as organic matter discharged from breweries, milk processing plants, paper mill, and municipal wastewater treatment plants are decomposed by oxygen-consuming bacteria. Concentration of the dissolved oxygen in the water body system is an indicator of the quality of water. BOD is the quantum of the amount of the oxygen needed to remove the waste organic matter by the decomposition process by the oxygen using bacteria. Decomposition of the organic wastes by the large population of bacteria results in the depletion of oxygen levels in water. This causes other aquatic organisms, such as fish, to die. The harmful algal blooms also become oxygen-demanding wastes, as these decrease the oxygen in water leading to hypoxia and form dead zones because the low oxygen levels cause death to the organisms that are not able to leave the environment. This will cause deoxygenation of water, thus when the organic waste in the water is high, then the oxygen in the water will be used up by the aerobic bacteria to decompose the waste causing anerobic condition to be present. Such conditions may be less visible in the rivers as its water is moving but can occur in lakes or slow-moving water bodies. BOD is often used as an amount of the degree of organic pollution in water of wastewater treatment plants.
3. Pharmaceuticals and personal care products (PPCPs) found in the waste are of concern as the products look for a way into the water, contaminating it. These products go into the environment through consumption and excreta of humans, and the sewage treatment plant is unable to treat these effectively. Thus, these get deposited in the water, which is consumed and can have varied and discreet effects on health. Pharmaceutical products may also enter in the environment due to improper and indiscriminate disposal, leaky sewer pipes, hospital and household waste, runoff of sludge fertilizer, and retrieved wastewater irrigation. The immense evidence from monitoring studies show that PPCPs are ubiquitous in the aquatic environment [12]. The extensive use of PPCPs globally combined with the enormous introduction of new pharmaceuticals to the market is substantially contributing toward the presence of these chemicals and their active metabolites in the aquatic environment. Although all PPCPs are not persistent, but their continuous presence in the environment means that some are thought as pseudo-persistent [13]. The presence of pharmaceuticals poses both acute and

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chronic threat to the aquatic life [14]. Extremely high concentrations of ciprofloxacin (31 mg/L) were measured in the effluent in Patancheru, near Hyderabad, India. It was found that ground surface and drinking water were immensely contaminated with pharmaceuticals [15]. These cause abnormal endocrine functions and increased cancer risks in humans [16]. Also called as EDCs, or endocrine-disrupting chemicals, may disrupt the endocrine functions in aquatic organisms and cause reduction in sperm and egg cell production and feminization of female aquatics organisms [17]. Not only are the aquatic organisms affected due to pharmaceutical contamination, aquatic plants are also impacted as these are taken up by the roots and get accumulated in the edible portion of the plant.

4. Pesticides/organic chemical pollutants: Different types of organic chemicals are used, but those posing serious threats to water and fish fall under the broad classification of pesticides. These include insecticides and herbicides. Also, the industries to deliver several organic pollutants and the unbridled disposal of these into waterbodies also contaminate water. DDT-containing organochloride is one of the pesticides used since 1900s to contain malaria. Other pesticides such as hexachlorobenzene, deltamethrin, parathion, and aldrin are used to control vectors that cause disease and to control the growth of unwanted and harmful organisms. These enter water bodies from agricultural fields runoffs thus polluting aquatic systems. Presence of low concentrations of diazinon, a backyard chemical, affects the sense of smell of salmon due to which it loses its ability to avoid predators [18]. As these are mainly nonbiodegradable so these persist for longer durations of time in the environment.
5. Sediments and suspended solids are fine grains of sand, clay, rock, soil, or other solid particles that settle or sediment at the bottom of water. These enter the water body due to soil erosion that may have happened in the vicinity or from decomposing plant and animal and is carried to the water bodies by water, wind, or rain. About 30% of this sediments occur due to the natural erosion, and 70% is contributed by accelerated erosion occurring due to the use of land by man. Agricultural activities, dredging, and construction business are the major contributors of sediments as pollutants in wastewater. All such activities cause erosion of land resulting in loosening of the soil cover. Certain types of farming also cause erosion. Removal of grass and plants to cultivate crops loosens the soil, which is then easily carried away by water and wind. Soil is washed downhill by rain when hillsides are used for cultivation and farming. Soil gets exposed when construction or any other developmental activity is done. This loosened soil is washed away to the nearby lakes, rivers, and streams. Dredging or digging up channels for large boats to pass also stirs up sediments that are picked up by water currents and settle in other water bodies. Due to dredging, oyster beds get destroyed in the estuaries, while as in fresh water, dredging eliminates the organisms that are bottom dwelling on which the fish depend. Harmful chemicals get adsorbed or attached to these sediment particles and are transported into water bodies [19]. These pollutants contaminate the ecosystem of the water bodies,

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making their water murky preventing natural vegetation from growing. Chemicals transported by the sediments cause activation of blue-green algae, these produce toxins into the water [20]. Sediments clog fish gills and affect fish egg and larva development by burying the gravels nests in which these rest, thus decreasing growth rates. Sediment particles increase the temperature of water by absorbing the heat of the sun, thereby making the environment uncomfortable for the inhabitants.

6. Temperature changes that occur in water due to various reasons is also another form of pollution called thermal pollution. Also called as thermal enrichment, it is a sudden alteration in the water's ambient environment that causes degradation of water quality. Water used like a coolant by industries and powerplants return this water back to the environment, at an elevated temperature leading to death of fish and other organisms. The change in temperature by just 1°C or 2°C reduces oxygen level and affects the ecosystem of water bodies. The metabolic rate of the organisms increases, thus their rate of respiration increases, also the amount of dissolved oxygen is reduced. Higher temperature increases plant growth rate of primary producers such as plant and cyanobacteria, decreasing their life span. Reservoirs release abnormally cold water toward the water bodies which dramatically decreases the productivity of the river and thus eliminates the indigenous organisms such as inhabiting the aquatic ecosystem. Other sources of thermal pollution are electric and nuclear power plants, oil refineries, which release water at altered temperature causing changes in the chemical, physical and biological characteristics of the water bodies thus affecting the aquatic biota. It modifies the dissolved oxygen levels causing disruptions in the rates of reproductive, respiratory, and digestive systems of the inhabitants. Aquatic plants show reduced photosynthesis rate due to inhibition of enzyme activity with increased temperature. Fish and other fauna experience a temperature shock with changes in the temperature of water [21,67].
7. Oil spills happening in the water bodies and aquatic systems are mostly accidental involving pipelines, refineries, ship collision, and tankers carrying diesel, petroleum, or other such derivates. The spillage from tankers is large enough to adversely impact the aquatic ecosystem. These contaminate the aquatic bodies and have deleterious effects on fishes, birds, aquatic organisms, and vegetation. Since oil cannot dissolve in water, it forms a thick sludge that suffocates the aquatic organisms, it forms a thick layer on the surface of water called oil-in immersion and does not allow sunlight to pass through. The aquatic plants thus are not able to photosynthesis. Spills may take weeks to clean up [22,68]. The oil spills can interfere with the sense of smell and taste of some fish because the oil in water masks these. Due to this the fish are not able to recognize each other and unable to find their spawning streams and homes.
8. Presence of acids and bases in the effluents of industries and mining can drastically affect the standard of water in the streams and lakes, etc. these do not allow the aquatic organisms to perform their reproductive activities and in extreme situations can lead to their death. Sulfur dioxide and nitrogen dioxide released into the air by the burning of fossil fuels or volcanic activity react with

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oxygen of the atmosphere and hydrogen to form nitric acid and sulfuric acid in the air [23]. And fall to the earth in the form of rain or snow and enters the water ways, which carry this acid to the lakes and streams, thus contaminating the water. The acid rain that enters the water bodies, lowers the pH, and impacts the aquatic ecosystem [24].

## 3. Diversity of microbes in wastewater

Wastewater from different sources needs treatment process where microbes play the role of key factors leading the degradation of organic and inorganic substances present, recycling of nutrients, and production of alternate energy. Bacteria, protozoa, fungi, algae, viruses, and helminths are the major microbes available leading to biodegradation of toxic and recalcitrant polluting contaminants present, leading to the outspread of various water-borne illnesses.

### 3.1 Bacteria

Various bacterial species are reportedly present in industrial wastewater that can convert organic matter to simpler compounds. Bacteria are mainly 0.2–2.0 μm in size found mostly grouped in flocs possessing vital role in biological wastewater treatment. Bacteria are known to stabilize the waste material present during microbial treatment. Bacteria can form floc that results in the absorption of waste and can subsequently lead to the waste breakdown. Filamentous bacteria serve as a backbone for floc particles where particles will grow and can tolerate the shear forces while treatment is taking place. Numerous infectious bacteria are available in wastewater that can lead to various diseases such as dysentery, typhoid, gastroenteritis, and cholera [25]. The commonly present microbial pollutant is bacteria in wastewater. Treatment processes contain both autotrophic and heterotrophic bacteria, but majorly heterotrophic bacteria are found. The heterotrophic bacteria available in wastewater can degrade the carbonaceous organic matter to obtain energy and utilize this energy to synthesize new cells. Industrial wastewater mainly contains few important bacterial genera like *Enterobacter*, *Achromobacter, Alcaligenes, Escherichia coli, Arthrobacter, Citromonas, Serratia, Flavobacterium, Pseudomonas, Zoogloe,* and *Acinetobacter* [26,27,69].

### 3.2 Protozoa

Protozoa are unicellular organism that are quite huge when compared with bacteria that can feed on pathogenic bacteria, thus possess a very important role in wastewater-treatment processes. They can perform various functions in wastewater treatment, like clarification of wastewater effluent by bacterial removal, suspended materials flocculation, and act as biological indicators. Protozoa is broadly divided into five categories based on their mode of locomotion including ciliates (free swimming), crawling ciliates, sessile ciliates, flagellates, and amoeboids [28]. Few

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protozoan species need oxygen, others can survive on little oxygen, and some needs anaerobic conditions for their survival.

Protozoa is reported to secrete growth-stimulating substances to promote the bacterial activity. It can remove the organic material available in sewage and can mineralize carbon from the activated sludge. Activated sludge mainly consists of ciliated protozoa followed by flagellate protozoa and amoebae. *Aspidisca* sp. and *Euplotes* sp. (crawling ciliates) have cilia on its belly/ventral area and are mainly found on floc particles, *Litonotus* sp. and *Paramecium* sp. (free swimming ciliates) possess cilia all over their body, *Carchesium* sp. and *Vorticella* sp. (stalked ciliates) are attached to floc, and cilia is present around their mouth opening only. *Aspidisca costata, Chilodonella uncinata, Carchesium polypinum, Opercularia coarcta, Opercularia microdiscum, Vorticella convallaria,* and *Vorticella microstoma* are ciliated protozoa that are commonly available in wastewater-treatment systems [28,29]. Naked (*Actinophyrs* sp., *Mayorella* sp., and *Thecamoeba* sp.) and shelled (*Cyclopyxis* sp.) amoebae are also present in wastewater treatment technique that contain no protective layer in naked amoeba, whereas shelled amoeba contain covering made up of calcified substance [30,31].

## 3.3 Algae

Algae possess photosynthetic capacity and utilize solar energy for photosynthesis. It can also absorb nitrogen and phosphorus resulting in eutrophication. Algae possess various roles in the treatment of wastewater in which it can act on organic and inorganic contaminants and can accumulate heavy metals, pesticides, and nutrients. Various species of algae are commonly utilized for wastewater treatment including *Euglena* sp., *Chlamydomonas* sp., *Oscillatoria* sp., *Limnothrix* sp., *Synechocystis* sp., *Microcystis* sp., and *Lyngby* sp. [32]. Algae thus help in the decreasing the load of metal ions (nitrogen, phosphorus) from the wastewater that are utilized for generating biofuels (algal biofuel), food, feed, and pharmaceutical ingredients.

## 3.4 Fungi

Treatment of wastewater includes multicellular organism fungi that will hydrolyze organic compounds present and oxidizes ammonia into nitrite and further to nitrate. Even under low pH environments, where there is no bacterial population, the fungal strains can break down the complex organic matter. Moreover, certain species of fungi utilize their fungal hyphae for adsorbing and trapping suspended solids from the wastewater in order to fulfill their nutrient and energy needs. Some fungal species also secrete some enzymes that can help in degradation of substrates during wastewater treatment [33]. *Sphaerotilus natans, Aspergillus, Penicillium, Fusarium,* and *Absidia* are the commonly available fungus associated with the waste removal and will also result in the carbon and nutrient removal from the wastewater. Whereas *Sphaerotilus natans* and *Zoogloea* sp. are the most common sewage fungus organisms [34,35].

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### 3.5 Virus and helminths

Wastewater consists of large quantity of human viruses and comparatively smaller quantity of plant and animal viruses. These viruses can lead to various waterborne diseases and infections in humans like gastrointestinal and respiratory infections, conjunctivitis, and meningitis. These viruses will remain a source of infection for several months once entered the wastewater.

Nematodes indicate the condition of wastewater treatment system. No nematode activity represents a highly toxic condition of the treatment system. Nematodes are multicellular organisms available in the fresh, brackish, or salt water and present in soil (wet or humid) serving as food for small invertebrates [35–37]. They reach the floc, can move freely, and secretes sticky material. Helminthes reproduce through eggs that vary in shape and size. In wastewater treatment system, helminthes eggs are separated by physical technique like sedimentation, filtration, coagulation, and flocculation. Moreover, the eggs can be inactivated at enhanced temperature and lower levels of moisture conditions.

## 4. Role of microorganisms in industrial wastewater treatment

### 4.1 Paper and pulp industry

Paper and pulp industries are reported by various researchers to be a highly polluting industry that generates toxic wastewater. Chemical constituents including chlorinated compounds, lignin and its derivatives, adhesives, dyes, fillers, peroxides, ozone, etc. are released in the wastewater. During pulp making, pulp bleaching, washing, deinking in paper making, various recalcitrant, and harmful contaminants are produced. Pulping will amount to highest level of generation of polluting contaminants in the papermaking process. Therefore, treatment of wastewater by biological means that utilizes bacteria, fungi, as well as their enzymes produced are identified to be cost-effective and economical methods for degradation of toxic compounds.

In the past years, various microorganisms or enzymes from microbial sources are utilized in different biotreatment methods (biopulping, biobleaching, biorefining, and biological deinking) in paper industry for the biological degradation of xenobiotic pollutants. Biopulping will remove lignin and hemicellulose by enzymatic action [38] produced by fungi (white rot) such as *Corioulus versicolor, Ganoderma colossum, Phanerochates chrysosporium, Phlebiopsis gigantean, Physisporinus rivulosus, Trametes versicolor,* and *Schizophyllum commune* [39]. In comparison to traditional pulping techniques, biopulping results in decreased energy costs and environment issues. Whole microorganism or enzymes, such as xylanase, laccase is used in the bleaching technique for pulp in paper industry is called as biobleaching. Enzyme xylanase in bleaching can enhance the brightness of pulp, degradation of cellulose, enhances pulp properties, reduces kappa number, and the use of chlorine as bleach. Cellulase-free xylanase obtained from cultures of fungus and bacteria are suitable for pulp prebleaching. *Bacillus halodurans* FP135-producing xylanase enzyme by fermentation (submerged, solid state) process showed significant

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biobleaching of kraft pulp. It showed reduction of up to 30%–35% in kappa number, 20% reduction in chlorine requirement, and increase of up to 5.8% in brightness, respectively [40].

Deinking is the technique of removal of ink as well as dirt from the wastepaper, and it is regarded as the vital step of wastepaper recycling. Traditionally, deinking needs various chemicals like sodium hydroxide, sodium carbonate, sodium silicate, hydrogen peroxide, and surfactants, resulting in a costly treatment technique. The microbial enzymes individually or in concoctions such as amylase, cellulase, xylanase, hemicellulases, and lipases are found efficient in deinking. *Aspergillus nidulans* AKB-25-producing cellulase and xylanases used for deinking showed enhanced brightness of pulp, increased burst and textile index, and improved deinking efficiency as reported by Kumar et al. [41].

## 4.2 Textile industry

Textile industry is utilizing higher amount of water and produces large variety of harmful and recalcitrant organic compounds, surfactants, solvents, toxic dyes, and detergents. Various categories of dyes are utilized in textile industry, azo dyes being the most common ones. Presence of dyes in the wastewater impacts the flora, fauna, and fishes severely and finally influence human health and lead to allergies, tumors, and cancers. Thus, degradation of textile industry dyes from wastewater is on top priority, which includes various physical, chemical, and biological techniques [42]. Bioremediation using single culture of bacteria, fungi, algae, yeasts, actinomyces, or microbial consortia can be effective in treating several dyes. Numerous bacterial, fungal. and yeast pure cultures were used initially for decolorization of textile dyes. Bacterial strains such as *Bacillus cereus, Bacillus subtilis,* and *Aeromonas hydrophila* utilized in the form of pure culture for toxic azo dyes decolorization. Remazol Orange 3R, a commercial azo dye used in textile industry, is decolorized majorly by *Pseudomonas aeruginosa* strain BCH with very high efficiency (98%) in 15 min [43]. Similarly, genus *Halomonas* also shows various promising results. Fungal cultures including *Phanerochaete chrysosporium*, *Dichomitus squalens*, *Ischnoderma resinosum*, and *Pleurotus calyptratus* are most frequently used against the decolorization of Remazol Brilliant Blue R and Orange G [44]. Similarly, *Trametes pubescens* and *Irpex lacteus* are capable to decolorize the Congo Red and Isolan Dark Blue dye effectively [45]. Various yeasts from genus *Candida* are utilized for the biodegradation and decolorization of dyes due to their lower production cost and stability under extreme conditions. Remazol Black-B dye can be successfully removed using yeast, *Kluyveromyces marxianus* strain IMB3C.

Microbial consortia prove beneficial as the biodegradation and removal of dyes reached higher levels because of the synergistic metabolic activities among microbial strains. Bacterial consortia, such as *Pseudomonas*, *Arthrobacter*, and *Rhizobium* sp., were found effective against azo dye, Acid Orange 7 degradation with 90% efficiency in 96 h of treatment as reported by Ruiz-Arias et al. [46]. Similarly, consortium BDN including *Alcaligenes* sp., *Bacillus* sp., *Escherichia* sp., *Pseudomonas* sp., *Providencia* sp., *Acinetobacter* sp., *Bacillus* sp., *and Bacillus* sp. were able to

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degrade 100% of reactive azo dye in 24 h [47]. Another halophilic consortium VN.1 includes *Pseudomonas fluorescens*, *Enterobacter aerogenes*, *Shewanella* sp., *Arthrobacternicotianae*, *Bacillus beijingensis*, and *Pseudomonas aeruginosa* was reported to be 100% efficient in degrading Reactive Blue 220 dye after 30 h of treatment [48].

## 4.3 Food and beverage industry

They are the largest contributors to growth in terms of turnover, employment, and financial and social significance. The processing of various raw materials leads to huge amount of wastewater containing diverse organic, inorganic substances that will pose serious health hazards on human and animals and ultimately ecosystem [49]. Waste is produced before storage, during storage, and during processing of raw materials in food and beverage industry. This waste includes mainly starch and sugars acting as primary carbon source.

Beverage industry is broadly divided into three major types including brewing, distilling, and manufacture of wine. These industries generate mainly liquid waste with high levels of BOD and COD. The fermentation units produce higher concentrations of phenols, tannins, and organic acids in the wastewater. Various fungal cultures, such as *Mycelia sterilia, C. versicolor, G. candidum, Trametes vercicolor*, and *P. chrysosporium*, are utilized for wastewater treatment containing phenols. *Candida* sp. resulted in decreasing the phenol content and COD by at least 50%. On immobilization of *C. versicolor* in packed bed reactor, the COD was reduced to 77%. Yoshi et al. [50] reported 90% reduction in COD and BOD when *Geotrichum* sp. is used for the treatment of distillery wastewater of an alcoholic drink (Shochu). Fungal biomass protein production and COD reduction were analyzed for the treatment of waste from winery industry using three fungal cultures like *T. viride* WEBL0702, *Aspergillus niger* WEBL0901, and *A. oryzae* EBL0401 [51]. *T. viride* WEBL0702 was selected based on results due to its less nitrogen needs and higher level of productivity.

In food industry, washing of potato and other similar tubers will generate effluents rich in sugar, starch, and proteins containing higher BOD levels and huge number of suspended solids in wastewater. Microbes like *C. utilis* and *Saccharomycopsis fibuligera, Cellulomonas* sp., and *Bacillus* sp. are utilized in food processing industry effluents effectively. For the treatment of wastewater from potato processing unit, various bacterial cultures including *B. acidocaldarus, B. coagulans, B. stearothermophilus*, *B. brevis*, *B. licheniformis,* and *Lactobacillus* sp. are used. These strains were found efficient in decreasing the total solids, starch content, and BOD level of wastewater via thermophilic aerobic digestion process in 96 h of treatment [52]. Wastewater produced by olive mills is of major environmental concern due to the higher organic fraction mainly containing phenolic compounds that are difficult to degrade. Other compounds include lipid, sugar, tannin, polyphenol, pectin, and polyalcohols. Microbes like *Bacillus pumilis* and *Azotobacter vinelandii* showed significant reduction in the phenol concentration in wastewater produced by olive mill [53].

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## 4.4 Pharmaceutical industry

Pharmaceutical industry generates wastewater containing mixture of diverse compounds (organic and inorganic), solvents, steroids, hormones, antibiotics, residues of active pharmaceutical ingredients, and other toxic chemicals that poses great challenge in its proper treatment. Wastewater contains numerous pharmaceutical agents, hormones, and antibiotics utilized in human and veterinary medicines including diclofenac, ibuprofen, naproxen, fluoxetine, 4-aminophenol, erythromycin, triclocarban, trimethoprim, diphenhydramine, estrogen, progesterone, testosterone, and androgens [54]. These contaminants are present not only in industrial wastewater but also in domestic, surface wastewater, and ground water sources.

Various treatment techniques for pharmaceutical wastewater include oxidation, ozonation, Fenton reactions, perozonation, ultrasonic irradiation, and bioremediation. Microbial remediation is a cost-effective and ecofriendly approach, which allows dealing with huge number of pharmaceutical contaminants compared to chemical and physical techniques. Fungal strain *Tramates versicolor* can successfully remove antibiotics (ibuprofen, naproxen), antiinflammatories, analgesics, and psychotropic drugs [55]. Dyes can be efficiently treated using cultures of *Chlorella vulgaris, Candida tropicalis, C. zeylanoides*, and *Debaryomyces polymorphus*. Metal ions such as copper, zinc, and iron and organic matter in wastewater are efficiently removed by *A. oryzae, A. variabilis, Tolypothrix ceytonica,* and *Anabaena doliolum* [56]. Table 3.1 represents various microbes involved in the removal of contaminants of pharmaceutical wastewater.

**Table 3.1** Microbes involved in the removal of contaminants from pharmaceutical wastewater.

| Microbial sources | Pharmaceutical contaminant removed/ evaluated | References |
|---|---|---|
| *Penicillium decumbens, Penicillium lignorum* | Reduction in COD, phenol, and color | [57,58] |
| *Bjerkandera adusta* MUT 2295 | 91% COD reduction | [59] |
| *Pseudomonas, Enterobactor, Streptomonas, Aeromonas, Acinetobactor,* and *Klebsiella* sp. | 44% COD reduction | [60] |
| *Pseudomonas putida* MTCC 1194 | Phenol<br>Catechol | [61] |
| *Pseudomonas fluorescence* | PhenolChlorophenols | [62] |
| *Phanerochaete chrysosporium* | Degrade ibuprofen and diclofenac | [63] |
| *Pseudomonas* sp. CE21 | Cefalexin, sulfamethoxazole, caffeine, salicylic acid, chloramphenicol | [64] |
| *Bacillus thuringiensis* B1 | Ibuprofen, naproxen | [65] |
| *Paracoccus* sp. T231 | Trimethylamine, dimethylamine, methylamine | [66] |

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Wastewater treatment utilizing microorganisms depends on various physical and chemical parameters like temperature, pH, retention time, level of dissolved oxygen, organic compounds present, and toxic chemicals present. Combinatorial approach gives better results for wastewater treatment in which microbial treatment is combined with other feasible physicochemical techniques of advanced oxidation process.

## 5. Conclusion

Industrialization resulted in revolution across all the nations due to its immense benefits for human life. But simultaneously it raised various issues related to generation of several toxic and recalcitrant compounds in the wastewater that has harmful impact on flora, fauna, and the complete ecosystem. Therefore, we require continuous monitoring of the characteristics of waste generated by these industries and to work upon the best possible techniques for their degradation. Wastewater treatment by biological method is a significant treatment technique for a variety of polluting substances when compared to the physicochemical techniques due to its eco-friendly and cost-effective approach. Microbial culture individually or as consortium and microbial enzymes attracted various scientists and researchers across the globe and is considered to be the highly sustainable technique as it results in the formation of a nontoxic end product.

Wastewater treatment via microbes is also beneficial as microbes are easily manipulated, modified, and studied. They constitute a simple model of biological system that can be analyzed for its growth, metabolic regulation, behavior, adaptation, and pathways and networks. Microbial enzymes have specific role in catalysis, and thus have immense role in the degradation of toxic contaminants. The diversity of pathogens present in industrial wastewater raises concerns about the role of microbial culture selection in the biodegradation process. So, further studies are needed to analyze the impact of specific microbial communities on the industrial wastewater for their future application in wastewater degradation studies for the elimination of the emerging pollutants.

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CHAPTER

# Membrane-integrated BES for wastewater reclamation

4

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## 1. Introduction

Modern civilization, urbanization, and industrial innovation require huge quantities of water and energy, and are also responsible for the production of wastewater. Furthermore, depletion of natural resources, global warming, increasing population, and pollution have resulted in water and energy scarcity. Wastewater generated by various industrial, agricultural, and domestic sources is a serious concern to environmental and public health. Wastewater consists of various emerging contaminants, including heavy metals, dyes, waste catalysts, pharmaceutical compounds, volatile organic compounds, phenolic compounds, sludge, oils, pathogens, etc.

Treatment of wastewater or reclamation of wastewater is essential to meet the current demand for water supply as drinking, irrigation, potable, and process water. There are various conventional and advanced techniques for wastewater treatment, such as flocculation, coagulation, adsorption, membrane filtration, oxidation, ozonation, electrocoagulation, microbial degradation, etc. Treatment of wastewater using any of these techniques consumes large amounts of energy. For instance, the energy requirement for domestic wastewater treatment using an activated sludge process is about 0.6 kWh per cubic meter of wastewater [1]. Therefore, an energy-efficient and sustainable wastewater treatment technology, which also produces energy as a byproduct, is an emerging field of research that can work towards the issues of environmental protection and resources shortage. The bioelectrochemical system (BES) is a potential alternative in this regard. This process can treat wastewater with generation of electrical energy that can be obtained by utilizing thermal and chemical energy associated with the wastewater.

The microbial-electro remediation technique or bioelectrochemical system is an efficient technique for wastewater treatment using electrochemically active microorganism with energy capturing capacity. One of the most attractive features of BES is energy recovery in the forms of electricity, ethanol, hydrogen, hydrogen peroxide, methane production, etc., with comparatively less sludge production. BES has



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various advantages over the conventional wastewater treatment techniques. BES is a self-sufficient technique that can treat wastewater with low energy consumption and has diverse applications such as hydrogen production, nutrient removal, and desalination. The features of BES, its working principal, and membrane-integrated BES are discussed in this chapter.

## 2. Bioelectrochemical system (BES)

Wastewater treatment combined with energy recovery is the primary function of BES. Enhanced and efficient treatment of wastewater can be achieved by BES, which involves diverse reactions at the electrode site [2]. Transfer of electrons from substrate to electrode and electrode to substrate take place due to exoelectrogen microorganisms by virtue of extracellular respiration. Moreover, these exoelectrogen microorganisms are responsible for the degradation of organic contaminants in wastewater. Therefore, the main advantage of BES over conventional microbial degradation processes is the electrode-microbial metabolism via extracellular electron transfer for generation of electricity. Several types of microorganism are used in this process. The most common bacteria used in BES for degradation of contaminants are *Geobacter* and *Shewanella* [3]. The electrode may behave like a biotic or abiotic, and this depends on the target mechanism type.

BES has the ability to treat a wide spectrum of wastewater, ranging from low biodegradable to high biodegradable compounds, nitrates to sulfate azodye molecules, metals and resource recovery (nitrate, struvite compounds, etc.), recalcitrant compounds, etc. [4]. In BES, electrochemical and bioelectrochemical (direct or indirect anodic oxidation) reactions are also responsible for improved removal efficiency. However, these reactions are strongly dependent on electrode potential and biopotential. In BES with biofilm, the contaminants are treated by facilitating the extended exposure to microorganisms by the substrate (holding the biofilm matrix). Study of BES requires some of the basic concepts of electrochemistry, biochemistry, cell biology, chemical engineering, and physics [5]. Conventional BES can be categorized on the basis of the mode of biocatalyst activity and its form.

BES can be broadly classified as microbial fuel cell (MFC), microbial electrosynthesis cell (MESC), microbial desalination cell (MDC), microbial electrolysis cell (MEC), biophotovoltaics, enzymatic fuel cell, and bioelectro Fenton system [5,6]. All classes of BES have different key functions. MFC is mainly used for electricity production, MDC is counted for recovery and desalination, organic compound formation by reduction of carbon dioxide is the function of MESC, whereas hydrogen generation is the key function of MEC [6]. Biophotovoltaics systems utilize photosynthetic microbes (microalgae, cyanobacteria, etc.) for photolysis of water [7]; whereas, bioelectro Fenton systems utilize the Fenton process for wastewater treatment and MFC for power generation [5]. MFC basically consists of two anodic and cathodic chambers that are equipped with anode and cathode, respectively. Waste degradation and electric power generation takes place due to the exoelectrogen

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microorganism and transfer of electrons. MEC can be obtained by applying an external voltage to the electric circuit of a MFC. Here, the main advantage is production of carbon free and clean fuel, i.e., hydrogen. When the MFC is upgraded and coupled with the addition of a chamber for the desalination of water, then the whole assembly can be termed as MDC, which works on the same principal of electro-dialysis. One of the advantages of MDC over electro-dialysis is the bio energy production and low energy consumption. In MESC, several compounds such as methane, ethanol, and acetate can be produced by reduction of carbon dioxide and use of bioelectricity. Among all BESs, MFC is the basic and most utilized one. MFC have been reported as the most studied BES, which can be utilized for multiple applications such as treatment of wastewater, bioenergy production, contaminants sensing, etc.

Although BES provides excellent efficiency in containment removal with less sludge discharge/effluent, nevertheless, this effluent still requires further treatment prior to reuse or discharge in the environment. Moreover, use of simple substrate limits its application for the treatment of complex wastewater. All these issues can be resolve by integrating appropriate substrate or separator like membrane with BES, which provides reclamation of water along with high quality sludge/effluent and improved recovery as well as efficiency. Therefore, the conventional BESs are upgraded with membrane integration to obtain energy self-sufficiency and high quality sludge/effluent. Membrane-integrated BES is discussed in the following sections.

## 3. Membrane-integrated BES (MIBES)

Recently, membrane-integrated BES has gained more attention due to its diverse nature. In addition, integration of membranes in BES has been reported to be a more robust hybrid technic for sustainable water and energy reclamation. It exhibits high recovery rates and efficiency for wastewater treatment and reclamation as compared to conventional BES. Initially, MIBES was examined in activated sludge processes where the aerobic biofilm membrane acted as a self-sustainable and low-cost catalyst. In that study, it is reported that the MIBES can significantly overcome the drawback of conventional BES system [8]. Furthermore, MIBES can significantly improve the COD removal efficiency, biomass retention time, and recovery of electrical energy, and lower the oxygen consumption for COD removal. Performance of MIBES strongly depends upon the type of membrane used. Different membranes possess different permeability behaviors for permeation of water and ions, which depend on the membrane properties and characteristics. Various MIBES, types of membrane used in MIBES, and configurations are discussed in this section.

### 3.1 Types of membranes for BES

Generally, membranes with ionic or ion exchange properties are used in BES in order to provide ion transport through the membrane. Ionic membranes that can be integrated in BES are usually grouped on the basis of their porous structure or

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pore size, such as forward osmosis (pore size <1 nm), ultrafiltration (pore size <1 μm), dynamic membrane (pore size >1 μm), and gas permeable membrane (≈dense). Integration of these membranes can be through internal configuration or external configuration. Integration of different types of membranes is discussed in this section.

### 3.1.1 Dynamic membrane (DM)

Dynamic membranes are also referred to as secondary membranes, and are also known for their in situ formation techniques. DM can be formed by the deposition of a colloidal substance of mixed liquor in situ on a substrate. Generally, nonwoven cloth or stainless steel mesh is used as substrate. DM possesses large pore size and provides less fouling, easier maintenance, and comparatively lower cost than other membranes, the last being due to the use of an economical substrate. Submerged configuration is usually chosen for DM due to the direct formation of membrane by mixed liquor on substrate [8]. Integration of dual function (as membrane and electrode) conductive material is used in order to increase the BES performance. In DM-integrated BES, biofouling on substrate plays an important role as it contributes to the performance of BES by enhancing catalysis for oxygen reduction reaction and function as a biocathode. As DM comes under the pressure driven membranes, trans-membrane pressure will also affect the BES performance. MIBES with DM exhibits good efficiency for desalination, wastewater treatment, and water reclamation.

### 3.1.2 Ultrafiltration (UF) membrane

UF membranes are capable of removing pathogens, viruses, bacteria, suspended solids, or particles larger than 20 kDa molecular weight. Due to its small pore size (<1 μm), it can exhibit good permeation rate through the membrane. UF membranes are useful for the retention of biomass, which in turn is beneficial for slow biological processes like nitrification or denitrification, methanogenesis, etc. A compatible treatment plant with reduced sludge production can be obtained by integration of UF with BES. Furthermore, it provides high quality treated water. UF membrane can be coupled with BES in an internal or external manner. In internal configuration, UF membranes can be used as a separator or filtration component in the anode or cathode chamber. Use of UF in the anode chamber can lead to an increase in fouling, rapid trans-membrane pressure, and difficult in situ cleaning of fouling [8]. All these parameters limit its installation in the anode chamber. However, the problem of fouling can be reduced by introducing fluidized activated granular carbon, which maintains the trans-membrane pressure. Integration of UF in the cathode chamber can efficiently increase BES performance with reduced fouling. Less microbial growth results due to the use of anode effluent as a catholyte [8]. Moreover, aeration in the cathode can control the fouling rate with supply of electron acceptors. External coupling of membrane with BES involves integration of membrane bioreactor with BES. Generation of sludge can be reduced by this configuration. All these characteristics of UF membranes make it more suitable for integration with BES for high efficiency.

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### 3.1.3 Forward osmosis (FO) membrane

FO membranes works on the principal of a concentration driven process, in which water molecules pass across the semipermeable membrane form low to high concentrated solution by the virtue of an osmotic pressure gradient. FO membranes are more energy efficient and less prone to fouling as compared to ultrafiltration, reverse osmosis, and nanofiltration membranes. FO membranes can retain a wide range of contaminants due to very small pore size (<0.3 nm) [9]. Treatment of wastewater using FO membrane requires use of draw solution (saline water, sea water, ammonium solution, etc.) in order to generate driving force and osmotic pressure gradient. FO membrane can be associated with BES in two configuration, i.e., internal and external, similar to the previously mentioned membrane configuration. Internal configuration involves the immersion of the membrane cell in the anode or cathode chamber, whereas external configuration involves the hybridization of the membrane bioreactor with BES. MIBES with FO membranes significantly increases the performance of conventional BES.

### 3.1.4 Gas permeable (GP) membrane

Nutrient gas recovery from MIBES is obtained by involving gas permeable membranes with BES. Gas permeable membranes allow the passage of gas molecules only, while other molecules are retained on the other side of the membrane [6]. These membranes work on the basis of separation by a trans-membrane chemisorption mechanism. One example of the GP process is the recovery of ammonia form urine. In this process, ammonium ions diffuse from anode to cathode, where a high pH catholyte may convert the ammonium ions to ammonia gas. A hydrophobic gas permeable membrane then diffuses ammonia gas, followed by absorption by sulfuric acid [10]. GP membranes can also be used to supply oxygen to the cathode and reduce the energy consumption by controlling the aeration rate.

## 3.2 Classification of membrane-integrated BES

Similar to BES, MIBES are broadly classified as microbial fuel cell, microbial desalination cell, and microbial reverse electro-dialysis cell. Removal of salinity is efficiently achieved by microbial fuel cell and microbial desalination cell types [11,15]. All classes work on the same principal as that mentioned in the previous section for BES classification.

### 3.2.1 Microbial fuel cell (MFC)

In MFC, chemical energy is converted to electrical energy by means of exoelectogens. MFC consist of two chambers, separated by a membrane interphase. These two chambers are knows as the anode chamber and cathode chamber, as represented in Fig. 4.1. In the anode chamber, the anode electrode is mounted with electrochemically active bacteria where feed water (low conductive organic wastewater) is supplied. The second chamber contains the cathode electrode, which receives the draw solution. During the oxidation of organic compounds, electrons and protons are

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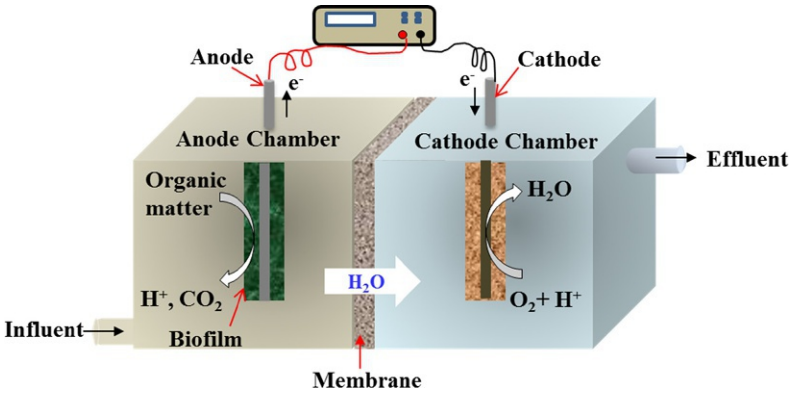


**FIG. 4.1**

Pictorial representation of a membrane-integrated microbial fuel cell (MFC).

engendered in the anodic chamber, followed by their transport through an external electric circuit to the electron acceptor and, thereafter, transfer of cations to the cathodic chamber through electrolyte or separator or membrane (ion exchange, FO) [12]. In this way, electric energy is generated in the anode chamber due to the anodic oxidation and cathodic reduction of organic compounds in the presence of electrochemically active bacteria, where an integrated membrane provides the recovery of water from wastewater. Permeation of protons or ions across the membrane results in enhanced recovery and removal efficiency. Osmotic microbial fuel cell and pressurized filtration microbial fuel cell are two categories of membrane-integrated MFC.

An osmotic microbial fuel cell can be obtained by combining the process of a forward osmosis (FO) membrane with the microbial fuel cell. The basic difference between conventional MFC and osmotic MFC is the use of an FO membrane in the place of ion exchange membranes. It also consists of a two stage configuration (anode and cathode chambers), which are separated by FO membranes. Electrochemically active bacteria play a major role in wastewater treatment and electric power generation. These bacteria are coupled with the anode electrode, which provides degradation and oxidation of organic compounds present in wastewater [11,16]. Electron and proton transfer occurs via the FO membrane, hence, size and selectivity of FO membrane also contributes to separation and enhances the proton or ion permeation rate. Salinity gradient or concentration difference is the major driving force in MFC. Membrane resistance can affect the rate of electric energy production. On the other hand, electrostatic repulsion is also responsible for the ion permeability and current generation. The basic configuration of osmotic MFC consists of a two-chambered design, as with conventional MFC. Recent advances in osmotic MFC have covered the use of different membrane materials and electrode materials, such as polyamide membrane, cellulose triacetate membrane, thin film composite membranes, air cathode, aerobic bio cathode (with air diffuser), etc.

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Pressurized filtration microbial fuel cell incorporates the use of pressure-driven membranes such as ultrafiltration, microfiltration, and dynamic membranes. These can be referred to as membrane bioreactors, bioelectrochemical membrane reactors, ultrafiltration MFC, anaerobic membrane bioelectrochemical reactors, etc. [11]. Pressure-driven MFC have a similar configuration to conventional MFC. The only difference is the existence of a pressure-driven membrane in pressurized filtration MFC. The integration of a pressure-driven membrane with microbial fuel cells provides highly efficient wastewater treatment. The basic mechanism of pressurized filtration MFC involves the initial treatment of influent by electrochemically active bacteria, followed by passing it across the membranes for further recovery or removal. As pressure-driven membranes are used in this type of system, the requirement of low-level hydraulic pressure is essential. Energy generation in this system is obtained by the cathodic reduction and bio anodic oxidation reactions of organic compound in wastewater. Significant reduction of COD, bacterial or viral contamination, nitrogen, suspended solids, etc., with generation of high quality potable or reusable water can be obtained by pressurized filtration MFC [12].

Pressurized filtration MFC may have diverse configurations, such as rectangular, cylindrical, tubular, two chambered, single chamber, or multichambered. On the basis of installation of membrane filtration in MFC, three basic configurations of pressurized filtration MFC are reported by Yang et al. (2019) [11]. These configurations include membrane filtration in aerobic cathode chamber, separation of two chambers by membrane filtration, and membrane filtration equipped in single chambered MFC. In the first configuration, MFC electrodes can be either submerged in the membrane bioreactor or installed as a membrane filtration module in the cathode chamber of MFC. Use of a dual functional conductive membrane also enhances the reactor performance by working as electrode and filter at the same time. The second configuration involves the use of membrane filtration as a physical separator between anode and cathode chambers of MFC. Usually, UF membranes are used for this purpose and can be referred to as ultrafiltration MFC [11]. In this configuration, wastewater is treated by electrochemically active bacteria (in the anode chamber) followed by filtration by the ultrafiltration membrane. The water permeation flux through the membrane is also responsible for the migration of protons from anode to cathode, which in turns leads to high electric energy production. The third configuration deals with the installation of membrane filtration in single chambered MFC. This can be obtained by either replacement of the anode and cathode electrode by conductive membrane or installation of a membrane module in the single chamber MFC. Limitations associated with pressurized filtration MFC are membrane fouling and control of transmembrane pressure.

### 3.2.2 Microbial reverse electro-dialysis cell

A microbial reverse electro-dialysis cell consists of ion exchange membranes, which promotes self-sustainability and power generation by virtue of salinity gradient. It also consists of two chamber assembly, as does MFC. The only difference between MFC and microbial reverse electro-dialysis cell is the reverse electro-dialysis stack

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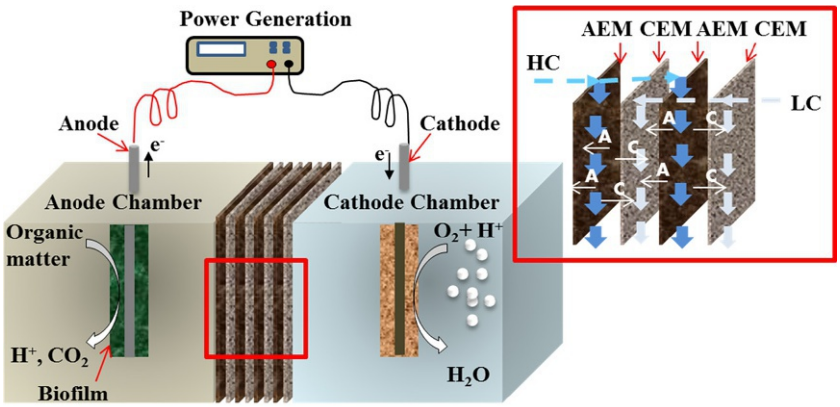


**FIG. 4.2**

Schematic of microbial reverse electro-dialysis cell with reverse electro-dialysis stack.

in between the cathode and anode chambers, as shown in Fig. 4.2. Ion exchange membranes are usually utilized for the reverse electro dialysis stack [13]. As represented in Fig. 4.2, the incorporation of the stack in between anode and cathode chambers results in separation of high concentration and low concentration cells. The concentration difference in microbial reverse electro-dialysis cell acts as the driving force for the transportation of anions and cations through the membrane. At the same time, anodic oxidation at the anode chamber and cathodic reduction at the cathode chamber generates the bioelectricity. Hence, the concentration-driven potential from the stack generates comparatively increased electric energy [13,17]. On the other hand, production of hydrogen gas occurs due to the salinity-driven potential capturing.

Conventional microbial reverse electro-dialysis cell has a similar configuration to MFC with reverse electro-dialysis membrane stack (Fig. 4.2). The reverse electro-dialysis stacks are comprised of different combinations of catalyst and electrodes, which can generate more hydrogen gas. Generally, electrodes are constructed of stainless steel mesh, which is coated with cathodic catalysts such as platinum, molybdenum disulfide, nonprecious metal catalyst, etc. [11] In the case of low concentrated feed or wastewater, external saline solution (e.g., ammonium bicarbonate solution) is used in microbial reverse electro-dialysis cell to establish a concentration gradient or saline potential gradient.

Limitations associated with microbial reverse electro-dialysis cell configurations include maintenance of pH and ion accumulation. These problems can be resolved by incorporation of bipolar membrane instead of anion exchange membrane. Incorporation of bipolar membrane also produces alkaline and acidic solution without any external energy sources. The problem of carbamate ion crossover in the anode chamber arises when ammonium bicarbonate solution is utilized in microbial reverse

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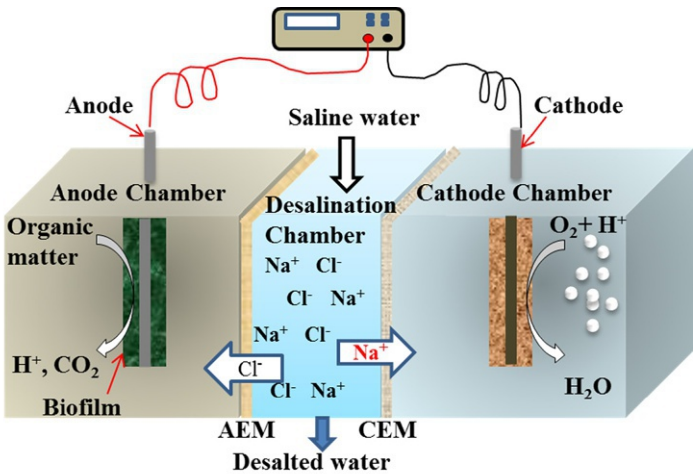
electro-dialysis cell. Formation of an additional low-concentration chamber beside the anion exchange membrane and filling of this chamber with anion exchange resin can efficiently reduce the carbamate ion crossover [11]. In this way, limitation of this type of MIBES can be overcome and can be modified accordingly.

### 3.2.3 Microbial desalination cell

Microbial desalination cell consists of an additional chamber, as mentioned in Section 2. These chambers are allocated by anion exchange and cation exchange membranes (Fig. 4.3). The main driving forces for this cell are salinity gradient (for dialysis generation) and osmotic pressure (for water permeation through ion exchange membrane). The organic constituents of wastewater get degraded by exoelectrogen at the anode chamber with the formation of electrons and protons. Migration of electrons to the cathode occurs through the external electric circuit, and that reduces the electron acceptor in the cathode chamber [11]. Along with electron migration, cations and anions of the desalination chamber also move across the ion exchange membranes, which in turn retains the total electric charge balance of the microbial desalination cell. This mechanism of microbial desalination cell provides desalination and electric energy generation without any external source of energy [11].

One of the important features of the microbial desalination cell is the proportionality between the desalination efficiency and electric generation, as the desalination efficiency increases with increase in current generation. Generally, three chambered rectangular configuration and tubular configuration is selected for microbial desalination cell, as shown in Fig. 4.3. The rectangular configuration has several design




*AEM = Anion Exchange Membrane; CEM = Cation Exchange Membrane*

**FIG. 4.3**

Schematic of a microbial desalination cell.

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limitations, such as accumulation of ions, pH imbalance, and low rate of desalination [11]. Rate of desalination can be enhanced by increasing the active membrane surface. Incorporation of multichambered microbial desalination cells can also enhance the cell performance by increasing the removal of ion pairs from saline water. pH imbalance in rectangular microbial desalination cells occurs due to the blockage of ion transport between cathode and anode chambers. This issue of microbial desalination can be eliminated by installing a direct pathway for proton transfer or maintaining neutral electrolyte pH in recirculation microbial desalination cell. The problem of ion accumulation can be prevented by inserting bipolar membranes, which can migrate the accumulated ions. Various developments and innovations are still required to enhance the performance of the microbial desalination cell.

## 3.3 Challenges associated with MIBES

Integration of membrane with BES system can potentially improves the reactor's properties, such as efficient and significant energy recovery, water reclamation, etc. However, although MIBES possesses several benefits over conventional BES, it has numerous challenging factors, which in turn need attention for the development of MIBES. The challenges are as follows:

- Membrane fouling is one of the major issues associated with MIBES. As the membranes are used to filter the ions from contaminated water, saline water, or wastewater chemical or bio fouling is very common in MIBES. The membrane fouling mechanism in MIBES is similar to conventional MBR. There is a possibility of deceleration of electric power generation due to the membrane fouling; on the other hand, electric power generation can also contribute to membrane fouling due to organic compound degradation and electric force generation. The reduction reaction in the cathode chamber may also result in biofouling on membrane surfaces; hence, limiting the reactor performance.
- Selection of membrane material or modification of membranes may increase the system performance. The selection of membrane material is another challenge that needs a detailed study before application. The fouling tendency of membranes can also be reduced by surface modification of the membrane by doping with effective polymer blends. Selection of low-cost and suitable membranes may reduce the cost of system.
- Scale-up of MIBES is another challenge related to the configuration of MIBES for real-life application. Integration of membrane can affect the economy of the system, which needs to compare with the existing technologies. Moreover, modeling and optimization can be effective tools to predict the system performance and scale-up.
- Issues exist related to low treatment efficiency for real wastewater and sea water. Treatment of real wastewater using MIBES results in lower power density and lower rate of COD removal as compared to synthetic wastewater. Therefore, there is a need to design MIBES adapted to overcoming this problem.

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## 3.4 Advantages and disadvantages

Self-sufficiency, efficient desalination properties, low sludge generation, flexibility towards design modification, smaller carbon footprint, comparatively high electric power generation, exhibiting less fouling tendency as compared to conventional MBR, capability towards nitrogen removal, and high quality of effluent are several advantages of MIBES as compared to conventional BES. Whereas, membrane fouling, high cost, ion accumulation on anode and cathode side, high internal resistance, insignificant scale-up studies, and unfavorable crossover of nitrogen are some of the disadvantages of MIBES.

## 3.5 Future perspectives and conclusion

MIBES is receiving more attention due to its versatile and diverse nature. Still, there is scope for research in the fields of reactor configuration, membrane material, electrode material, use of multifunctional membrane for specific applications, organic carbon source, use of suitable electrolyte, etc. [14]. Moreover, research can also be conducted in the direction of development of cell design, modeling and optimization for scale-up of reactor, mechanism for ion transport, design for real scale applications, reduction of fouling, etc. Other than these, studies have been carried out for different application of MIBES instead of only water reclamation, electric power generation, and removal of organic carbon, however, the field of study is open to other potential applications of MIBES such as water softening, toxicant removal, nutrient separation and recovery, pre- and posttreatment of desalination processes, and bio-sensors. Apart from these, safety issues related to the environment and human heath, as well as the techno-economic issues, needs to be considered for further research [14].

The integration of membrane with BES has expanded the field of application along with providing improved properties. Different types of MIBES can efficiently enhance electric power generation and water reclamation, and the configuration (anode chamber and cathode chamber) can be modified as per the requirement. Various challenges and advantages associated with MIBES may create a breakthrough and promising future for wastewater treatment industries, water reclamation, and power industries.

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CHAPTER

# Wastewater remediation for reuse through emerging technologies

5

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## 1. Introduction

The deficiency of superficial or ground drinking water for useable water production is of growing concern and attracts international attention. Wastewater, which is the biggest waste stream from municipal drainage, petrochemical and pharmaceuticals industries, food and beverage industries, textile industries, the agricultural sector, and polymer and paper industries, contain high levels of impurities such as oil and salts, and various organic and inorganic classes of contaminants [1–4]. However, in reaction to the water paucity, recycled wastewater is seen as a viable alternative water supply. As regards potable water recovery and processing, to our knowledge, direct reuse technology has been implemented only in Africa and Israel [5]. In contrast, indirect potable recycling has been widely accepted by introducing recovered water into surface or groundwater bodies. Soil aquifer treatment (SAT) is one of the most useful processes for indirect potable water reuse [6]. To improve wastewater quality, SAT can be used simultaneously with earlier advanced treatments.

Undoubtedly, the quality grade of treated water from a recharged aquifer depends on the introduced water. Artificial groundwater recharge is the most well-known practice, due to the additional treatment provided by underground transformations and because reclaimed water loses its identity as sewage water. However, human contact with reclaimed water puts higher demands on the WWT in order for the wastewater to be harmless for direct or indirect uses. Advanced treatment technologies have been used for enhancing the grade of domestic water in order to avoid potential effects of recalcitrant compounds. Due to the concern related to the presence of microcontaminants in water bodies, several researches on removal at wastewater treatment plants (WWTPs) have been accepted at full scale. Currently,



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conventional WWTPs largely achieve water quality in compliance with the various relevant regulations. However, municipal/industrial wastewater is a big and primary origin of microcontaminants in water streams [7]. The presence of microcontaminants is especially concerning if treated wastewater is being considered for reclamation. It has been seen that traditional biological treatment via activated sludge is not very effective for the removal of a number of such impurities. Thus, studies analyzing the effectiveness of conventional WWTPs with advanced treatment technologies are presented herein.

This chapter focuses on wastewater reuses following passage through various existing wastewater treatment technologies (WWTTs).

## 2. Advance technologies for wastewater remediation

In the past decade, various research groups have studied the efficiency of different advanced water treatment processes (WWTPs) for removal of contaminants of emerging concern to reduce the impact of discharges of reclaimed water from various water bodies [8]. In this chapter, we review several available technologies for the removal of micropollutants/nanopollutants showing their advantages and disadvantages. The selected technologies presented in this chapter (AOPs, MFT, ozonation, adsorption, desalination, nanotechnology) are those considered more established and ready to be functional as WWTPs [9].

### 2.1 Advanced oxidation processes (AOPs)

Generally, there are two steps that are usually deployed in WWT settings, consisting of pretreatment, involving mechanical and physicochemical systems to reduce the heterogeneous contaminants of the effluents, followed by an advanced treatment process. The physiochemical techniques boost the efficiency of the advanced treatment by agglomerating the pollutants into a bigger particle size for easy filtration or removal. However, degradation of emerging recalcitrant components with membrane and bioremediation in advanced treatment processes is complex. So, in addressing this problem, the AOP has gained much attention due to its huge potential to degrade an extensive range of organic micropollutants [10].

#### *2.1.1 Photocatalysis*

There are numerous semiconductors that are promising for water treatment, such as $TiO_2$, ZnO, $Fe_2O_3$, CdS, and ZnS, which are photoactive within a band gap energy of 2.3–3.2 eV and wavelength of 413–539 nm (shown in Table 5.1) [11]. The heterogeneous photocatalysis reactions, involve a sequence of reactions such as oxidation, dehydrogenation, hydrogen transfer, and metal deposition. In addition, the normal thermal and chemical catalytic actions that ease any distinctive chemical reaction require simultaneous activation of the molecules. As such, in photocatalysis, a light energy source with energy equal to or higher than the bandgap energy (eV) of the photocatalyst is deployed to excite the catalyst to be active during the reaction,

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**Table 5.1** Semiconductor photocatalysts and their band gaps at specific wavelengths ($\lambda$).

| Semiconductor photocatalysts | Band gap (eV) | Wavelength ($\lambda$, nm) |
|---|---|---|
| $TiO_2$ (Rutile/Anatase) | 3/3.2 | 413/388 |
| ZnO | 3.2 | 388 |
| ZnS | 3.6 | 335 |
| CdS | 2.4 | 516 |
| $Fe_2O_3$ | 2.3 | 539 |

bringing about the reduction or oxidation of the adsorbed species on the surface, for instance, oxidation of organic compounds into their subordinates until carbon dioxide and water are formed [12,13].

### 2.1.2 Disadvantages of AOPs

The main disadvantages of AOPs are their high chemical requirement and/or energy intake, which are reflected in high operating costs. Regarding the use of $H_2O_2$, there are significant limitations associated with its use. For example, the extra costs and complexities associated with chemical storage, handling, and injection may limit its attractiveness, and the residual $H_2O_2$ must also be quenched in some applications prior to environmental discharge.

With the present greenhouse emission problems and energy scarcity situation, photocatalysis emerges as one of the alternative ways of providing feasible solutions to the global challenges in relation to energy and the environment aspects. For instance, in the phenomenon of photosynthesis, green plants trap solar energy from sunlight and, with a series of enzyme catalyzed redox processes, convert the $CO_2$ into water and carbohydrates by releasing oxygen into the atmosphere, where most living organisms depend on it to survive. In this scenario, photocatalysis, which works with the same principle, has gained incredible attention and hence can be explored for various applications looking for sustainable energy, social economic growth, and environmental impacts.

## 2.2 Adsorption

Adsorption is a technology widely used in WWT, and several types of materials have been tested as absorbents. However, although there are a large variety of adsorbents in the market, most of the adsorption units in WWTPs use activated carbon, due to economic reasons. Adsorption is considered as a good option for the removal of microcontaminants due to the wide range of compounds that can be retained. The rate of adsorption of the microcontaminants to the activated carbon and the contact time will be key parameters for the final contaminant removal achieved. The first one is the function of the properties of both adsorbate ($K_{OW}$, p$K$a, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) [14].

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Novel functional materials based on biopolymers are of huge interest for water treatment as the hybrid materials offer attractive properties such as flexibility, low density, toughness, active surfaces, and high adsorption capability. BNCMs are also biocompatible, biodegradable, and environmental-friendly, and can be easily handled. The development of BNCMs/polymer adsorbent systems is highly encouraged nowadays because of their large removal efficiency and the spontaneous decontamination of water pollutants [15,16].

### 2.2.1 Polymer nanocomposites for adsorption

A composite can be defined as an assembly containing at least two or more nonmiscible materials forming a novel material with new properties that are quite different from those of individual materials. In recent years, biopolymer nanocomposites have fascinated the minds of many researchers because of their enhanced properties that fulfill the requisite requirements [17]. Some polymer nanocomposites preparation techniques are shown in Fig. 5.1.

## 2.3 Ozonation

Ozonation is an established technology, and the reactions involved in the method are well known. There are mainly two main reaction pathways for microcontaminants elimination by ozone. Ozone can react directly with organic pollutants through an

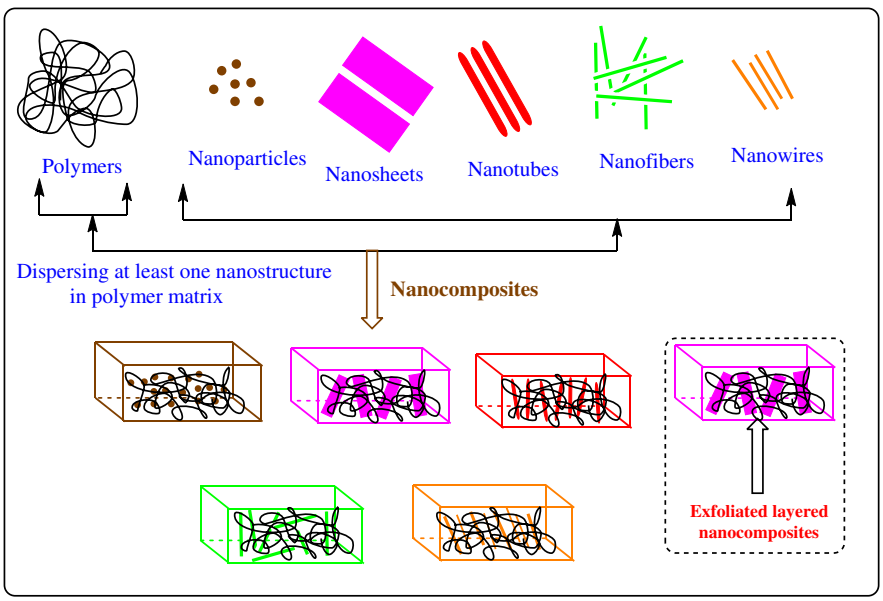


**FIG. 5.1**

Schematic diagram of polymer nanocomposites preparation.

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ozone molecular reaction mechanism. This reaction is quite slow and often selective. On the other hand, in alkaline waters, ozone can also react with the water or other bodies, forming highly oxidant hydroxyl radicals (HO·). Due to its instability and quick reactivity, ozone must be generated in situ using air or high-purity oxygen. Normally, the gas generated contains between 1% and 3% of ozone by weight if the initial gas is air, and between 8% and 12% if pure oxygen is used. Ozonation units in WWTPs for secondary effluent disinfection inject doses in the range of 3–30 mg ozone $L^{-1}$. After the generation, since the concentration of ozone is quite low, it is important to confirm a good contact between the gas and the water to ensure a good distribution of ozone and avoid over concentrations of ozone, which can lead to the formation of hazardous byproducts. Ozonation presents a reasonable cost of 0.16 € $m^{-3}$ compared to other tertiary treatments [18].

Due to the many ozonation units already functioning in different WWTPs, there are already some studies about the efficacy of ozonation to abolish microcontaminants completely. Furthermore, various studies can be shown at pilot plant level as examples of the use of ozonation at full scale.

The effects of ozonation after biological treatment for micropollutants elimination have been widely studied. Similar results are found if micropollutants are congregated according to their interaction affinity to react with ozone ($O_3$). There is a first group of compounds that are simply eliminated below detection limits with an average dose of ozone. Normally, those compounds present second-order type reaction rate constants ($\kappa$) $>10^4\ M^{-1}\ s^{-1}$ (regarding the straight reaction with ozone) such as substituents with aromatic rings, $\pi$ bonds, or amine groups, with a high binding/reaction capability for direct reaction with ozone gas [19]. There is a second group of compounds with low affinity for ozone but with great affinity for the strong and unselective hydroxyl radical (·OH). An average removal of around 60% was achieved for these substances. HO· radical exposure to microcontaminants varies with the composition (it is related to the addition of coagulants), presence of HO· scavengers (such as carbonate), and pH. Finally, there is a third group, which comprises those micropollutants with low affinity to $O_3$ direct reaction and also to hydroxyl radicals. These form a group of recalcitrant complexes with low removal (below 40%): atrazine, iothalamic acids, atenolol, diatrizoate, iopromide, mecoprop, benzotriazole, 5 methylbenzotriazole, sucralose, DEET, diazinon, galaxolidone, benzothiazole, micropollutants with amide (—$CONH_2$) groups in general, etc. [18,20].

## 2.4 Membrane filtration technologies (MFTs)

Membranes, as a thin film or layer barrier for various size differential separations (shown in Table 5.2), are typically included with chemical and biological treatments of wastewater [21–23]. In a characteristic membrane separation mechanism, driving force plays a central role; for example, a semipermeable membrane that controls the rate of transport of pollutant materials by fractional permeation and rejection through

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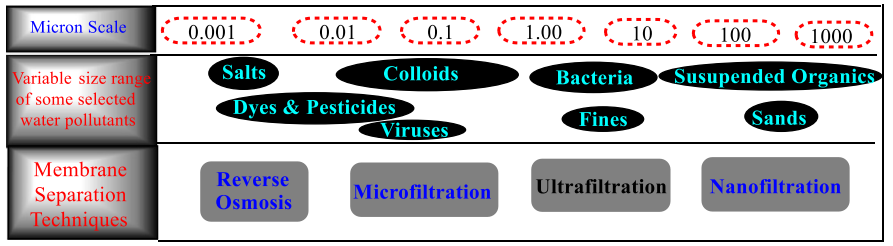
**Table 5.2** Effectiveness of each membrane technology for removing the different contaminants from wastewater as a function of their variable size range.




membrane pores of different sizes [24]. The permeation and specific rejection of the species is a function of the membrane pore size and chemical affinity. Fig. 5.2 shows various membrane separation processes.

### 2.4.1 Microfiltration (MF)

Microfiltration utilizes a sieving mechanism to retain macromolecular size, or large particles of more than 0.1 μm, selectively in the range of 0.1–10 μm [26]. Unlike UF, RO, and NF, the transmembrane pressure (TMP) for both sides of the membrane as a result of the small particle retention is tiny, hence requiring a relatively small TMP lower than 2 bar, but varies from 0.1 to 2 bar [27,28]. As indicated, the larger pore sizes of MF membranes specifically remove suspended solids, bacteria, some viruses (up to 2-log), protozoan cyst, turbidity, and to a lesser extent, organic colloids particles within the limits [27,29].

### 2.4.2 Ultrafiltration (UF)

The role of ultrafiltration (UF) is increasing as a pretreatment for desalination and membrane bioreactors. UF, like MF, utilizes physical sieving as a separation mechanism. The pore size, molecular weight cutoff (MWCO), and pressure for a UF membrane ranges from 0.05 μm to 1 nm, 1–500 kDa and functioning pressure is 1–7 bar [28,30]. As such, UF with a definite molecular weight cutoff (MWCO) is impermeable to compounds with molecular weights exceeding the range and have shown a 3–6 log removal of chlorine (Cl), resistant protozoan cysts, active *Giardia lamblia*, colloids, viruses, and coliform bacteria. The use of MF and UF as pretreatment to RO has gradually emerged as an industry standard. Both are often used as pretreatment for NF and RO processes to reduce membrane fouling and is also useful as a post-treatment to chemical precipitation for organic chemical removal and pH adjustment, as well as phosphorus, hardness, and metals removal [28–30]. Fouling is very common in UF due to the high molecular weight of fractions retained in relation

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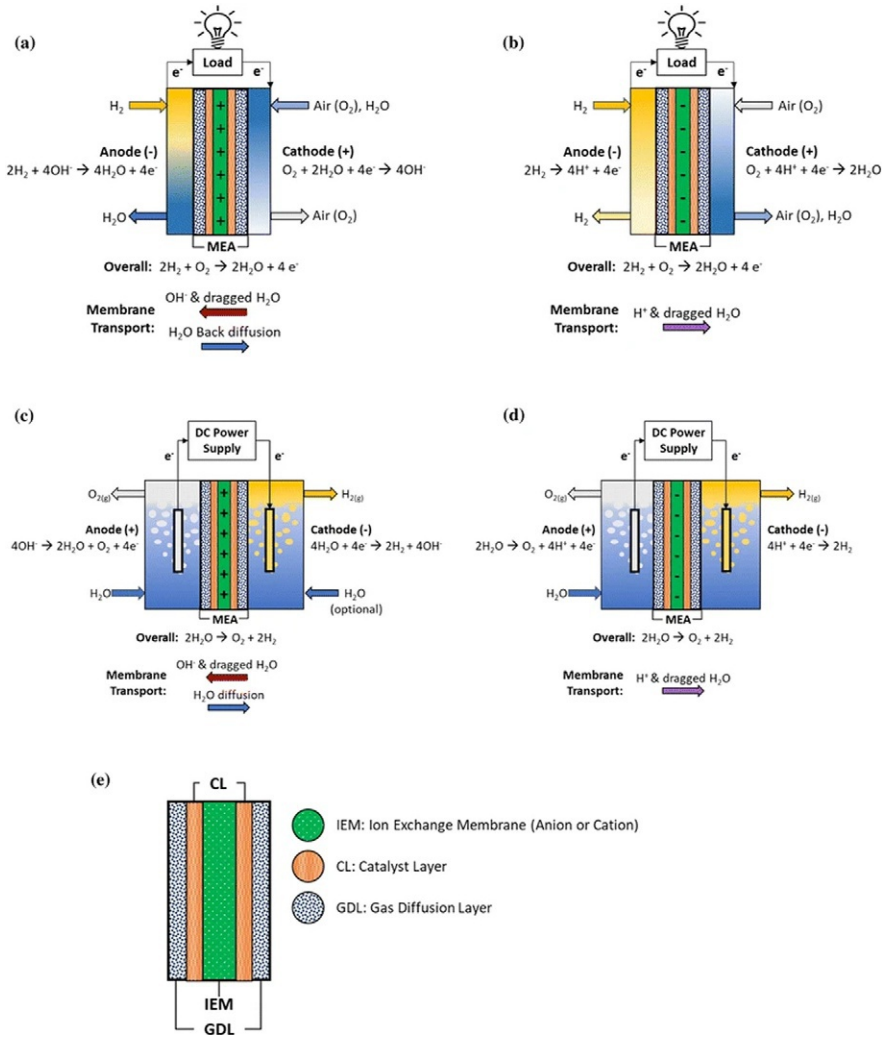


**FIG. 5.2**

Schematic representation of (A) anion exchange membrane fuel cell, (B) proton exchange membrane fuel cell, (C) anion exchange membrane water electrolysis, (D) proton exchange membrane water electrolysis, and (E) membrane electrode assembly [25].

to the small osmotic pressure differentials and liquid phase diffusivity. However, this does not negatively influence the demand for UFs, as any design, configuration, and application will be fouled [27,28]. The configuration for a particular application is influenced by the mechanical stability, hydrodynamic requirement, and economic limitations.

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### 2.4.3 Nanofiltration (NF)

Nanofiltration (NF) is a pressure-associated process where the separation mechanism is based on molecular size for the removal of dissolved microcontaminants and multivalent ions. NF is a complex procedure characterized by solvent diffusion, transport, and electrostatic repulsion effects at the membrane surface and within the nanopores [28,29]. The difference between the pore size and particle size forms the basis of the sieve effect. Based on the membrane pore size, NF is often referred to as loose RO, with separation taking place at the lower end of UF and upper end of RO, as it covers a pore size of 0.5–5 nm and operates at a relatively low pressure of 5–35 bar [27,28].

NF is usually deployed in the removal of polyvalent cations, reduction in color, tannins, and turbidity, and disinfection of byproduct precursors such as organic matter, as its potency lies in the high rejection of divalent ions (98%), permeation of monovalent ions (20%–80% rejection), and high flux. NF is often used as a post treatment or polishing step in conventional treatment processes. Although it is not recommended for use in desalination processes, it is used to reduce the salt content of slightly saline water. Recent applications have used NF as a pretreatment to RO, reducing the operating pressure in RO and providing savings in operational and maintenance costs [26].

### 2.4.4 Reverse osmosis (RO)

Reverse osmosis, often composed of tight membrane has been widely used in brackish water and WWT with its usefulness in desalination technology against conventional thermal Multi steps flash process. High external pressure of 15–150 bar, which is a function of the hypertonic feed and greater than the osmotic pressure, is applied to retain dissolved solute particles and solvent permeation around 100 Da through the diffusion mechanism [31,32]. Using the concentration gradient as the driving force, separation and concentration in forward osmosis (FO) occurs as the concentrated solution (e.g., salts such as NaCl) draws water from a less concentrated feed mixture solution. Characteristic advantages include low energy utilization, simple configuration and operation, low membrane fouling tendency, and high rejection of a broad range of contaminants. The use of FO is effective in ambient conditions, hence irreversible fouling is low [31,32]. However, FO technology is faced with the lack of recyclable and economical drawing solutions, internal and external concentration polarization, and a difficulty of developing effective bulk-scale plants [31]. To achieve the desired process flow and optimum configuration, ROs are prepared in stages and passes. The sequence of the steps has the concentrate stream of the first stage as the feed inlet of the second stage. Permeate streams from both streams are summed into one discharge channel. However, passes involve either a one path recovery of permeate or the rechanneling of permeates from the first RO into the second RO to improve quality.

Various membrane-based filtration technologies are shown in Table 5.3.

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**Table 5.3** The spectrum of wastewater treatment purification techniques and desalination.

| Filtration type | Pore size (nm) | Filter spectrum | Specialty |
|---|---|---|---|
| Microfiltration | >100 | High suspended solid | Sands, silts, organic particles, algae, fibers, fats, oils and grease |
| Ultrafiltration | 20–100 | Macromolecules | Microbiological species like bacteria, viruses, colloids, etc. |
| Nanofiltration | 0.8–3 | Small molecules | All types of bacteria, viruses, cysts, crystal materials, alkalinity, and hardness |
| Reverse filtration | 0.3–1 | Salts, ions, low molecular weight contaminants | All types of bacteria, viruses, cysts, pesticides, radium, and all inorganic pollutants |
| Ion exchange | 0.3–1 | Purifies and changes | Remove all metal ions, mineral contaminates to soften the water quality and its purity |

## 2.5 Biological wastewater treatment technology

Municipal solid wastes are becoming the subject of more obstructive regulation with respect to landfill disposal of the biodegradable portion. The treatment process for these organic parts is biological WWT. These technologies maximize the reprocessing and recovery methods of waste constituents. Biological treatment is regarded as a key and vital aspect of WWT and is a technique used in municipal/industrial fields for soluble organic compounds [33].

### *2.5.1 Anaerobic digestion (AD) process*

In the anaerobic digestion process, a large part of the organic matter (cells) is broken down into carbon dioxide ($CO_2$) and methane ($CH_4$), and this is performed in the absence of oxygen ($O_2$). About half of the amount is then transformed into gaseous molecules, while the remainder is dried and becomes a residual materials. Kougias and Angelidaki reported that the final products of organic assimilation in anaerobic treatment of waste are $CH_4$ and $CO_2$. AD technology has received significant recognition in the last few years with applications in separately configured high-rate treatment processes for industrial wastewater effluents [34]. In WWT setups, AD has been used in several instances throughout the world for bioremediation and biogas production. Other advantages of anaerobic systems include lower energy consumptions, a safer and more convenient way of converting "waste" to useful products (from trash to cash) associated with urbanization, being a prognostic tool for the fulfillment of the UN Sustainability Goal to meet global standards, having excellent

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nutrient recovery and high organic removal efficacies. Drawbacks of this process include longer hydraulic retention times (2–4 months) and high alkalinity requirements [34,35].

## 2.6 Desalination technology

Enhancing water security requires amazing adaptability and flexibility to handle with many avant-garde water treatment systems as well as using innovative flowrate approaches. For illustration, storm water, brackish or saline surface and groundwater, and industrial gray water were put into miscellaneous treatment methods for diverse utilization. Seawater is a vast resource that could provide water security. Unfortunately, seawater usually possesses high salinity, with total dissolved salts ranging from 35,000 to 45,000 ppm [36]. Wastewater also contains high total dissolved salts. Desalination is the process of eliminating the total dissolved salts from a variety of saline water gradients as well as wastewaters [37]. The methods of desalination are divided into two primary types: thermal process and membrane processes.

Thermal procedures for desalination are established on stage variations including: (i) multiphase flash distillation, (ii) multieffect distillation, (iii) vapor compression distillation, and (iv) humidification dehumidification. Membrane desalination uses membranes with unique properties. The major membrane methods include: (i) electrodialysis and electrodialysis reversal, (ii) reverse osmosis, (iii) membrane distillation, and others [37,38].

## 2.7 Nanotechnologies for heavy metals and metalloids remediation in contaminated water

Remediation methods for contaminated wastewater based on various available nanotechnologies are discussed in this section. The water remediation techniques include chemical precipitation, adsorption, cementation, electrodeposition, solvent extraction, UF, ion exchange, membrane filtration, bioremediation, phytoremediation, etc. (see Fig. 5.3). Removal of heavy metals and metalloids from contaminated groundwater can be achieved by (a) removal of the contaminants from the subsurface and (b) in situ treatment, where the contaminant metals are left in the subsurface and their mobility or concentration reduced to levels considered safe for the human body as well as the environment impact.

Chemical precipitation is one of the most commonly used remediation technologies for the removal of metals and metalloids from wastewater. It has advantage including effectiveness, simplicity of operation, and being economically cheap [39]. This technique is used for eliminating metallic cations as well as anions like fluoride ($F^-$), cyanide ($CN^-$), and phosphate ($PO_4^-$), as well as organic molecules. In precipitation, soluble heavy metals are transformed to insoluble metals, which settle and are filtered out of the water. Then a solid separation

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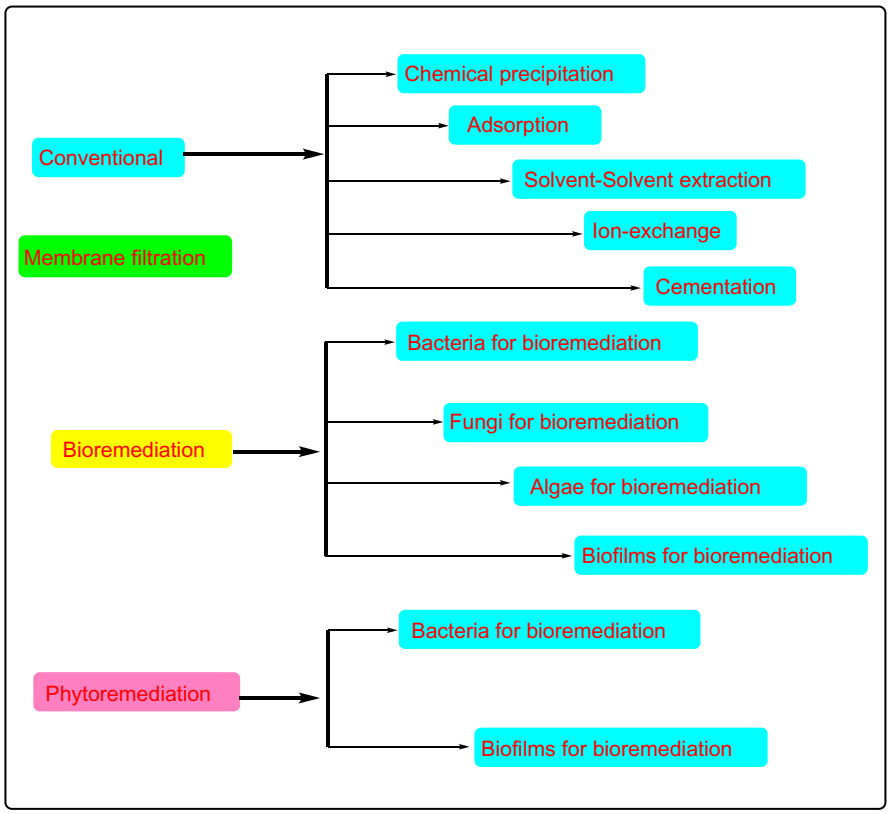


**FIG. 5.3**

A schematic representation of various nanotechnologies for the contaminated water remediation of heavy metals and metalloids.

process such as coagulation and/or sedimentation or filtration is followed by the conventional precipitation methods following two types of precipitation: (i) hydroxide precipitation and (ii) sulfide precipitation [40]. Between these two categories, generally, hydroxide precipitation is more commonly employed as compared to sulfide precipitation because it is easy to control, cheap, and easy to control its pH. Each of the soluble metals has a definite pH value that represents the optimum hydroxide precipitation.

Cementation is an effective and commercial hydrometallurgical process used as a means to recover toxic and valuable metals from solutions as well as for the cleansing process of stream and wastewaters in industry [41]. Cementation is a procedure in which a metal ion is precipitated from its salt solution to its elemental state by another electropositive state metal via a spontaneous electrochemical reduction

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process. This is associated with the consequent oxidation of a sacrificial metal to recuperate more expensive and noble metal species present in water solutions. The cementation method has some advantages like low cost, low energy accumulation, and recovery of metals in relatively pure metallic form, whereas the main disadvantage is that excess sacrificial metal is consumed in this process.

Bioremediation is a natural process, which consumes less energy as compared to other technologies in use. It is useful for the complete obliteration of a wide variation of impurities and can transform hazardous constituents to harmless stuffs. Biological approaches for the separation and detoxification of heavy metal ions and metalloids from contaminated water and sediments include several routes, such as volatilization, biosorption, leaching, precipitation, phytoremediation, oxidation/reduction, degradation, and bioaccumulation. In particular, recovery of heavy metals and metalloids is accomplished via biosorption using microbial and plant biomass/biomaterials [42].

Biosorption is achieved by using dead biomass, their constituents, and metabolites to cleanse heavy metals through physicochemical adsorption process. Conferring to the principle of biosorption, metal ions are interact with various forces such as van der Waals forces, complexation reactions, ion-exchange, electrostatic interactions, hydrogen bonding (H-bond), surface precipitation, or their combinations, and these forces or bonding interactions help in the adsorption process [43].

The bioaccumulation technique uses living microorganisms to absorb and eliminate heavy metals and metalloids taped in intracellular space. In bioaccumulation, the heavy metals accumulated in the microbial cells are precipitated or bound onto an intracellular assembly [44]. In particular, bioaccumulation is a naturally occurring biological process in which microbes use proteins to take up and store metal ions for later usage in cellular functions.

Oxidation/reduction reactions are used by microorganism species for detoxification and removal of metal ions. For example, Fe(II) and Mn(II) are removed by Fe(II) and Mn(II)-oxidizing bacteria following oxidation and precipitation methods by these microorganisms. Mn(II)-oxidizing bacteria and fungi react with manganese and produce manganese oxides, which have high desorption capacity for heavy metal cations, such as Cd(II), Cu(II), Co(II), Ni(II), Pb (II), and Zn(II). These bacterial- and fungal-generated manganese oxides are also capabale of oxidizing various inorganic compounds like Cr(III) and As(III) [45]. Arsenic is also oxidized by this manganese oxide from its As(III) oxidation state to As(V) state [46].

The leaching method involves biological procedures and products for the removal of heavy metals and metalloids from residues. Heavy metals in contaminated residues are removed via a solubilization process followed by microbial processes such as bioleaching and heterotrophic leaching technique [47]. Washing and removal of heavy metals in sediments using biosurfactants is also practiced. Bioleaching of mineral ores in bio-based industries is done by the acidophilic iron and sulfur-oxidizing bacteria *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*, respectively [47].

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## 3. Wastewater treatment for water security in the water-energy Nexus for developing countries

Climate change/global warming is changing the composition of the natural environment and has the most severe impact on world water resources. As stated by the Intergovernmental Panel on Climate Change, climate observation records and forecasts show that freshwater resources are susceptible to potentially being heavily affected by climate change with broader associations for human communities and ecosystems [48]. One of the crucial predictions of climate change, sea level rise, threatens the invasion of saline water into soil, and surface and groundwater especially in the coastal aquifers, being the primary line between the oceanic and terrestrial system and subjected to over exploitation [49]. South Asian coastal polders are extremely vibrant, with complex socioecological organizations including numerous poverty-driven vulnerable communities.

Despite the higher price and power requirements, prototype photovoltaics reverse osmosis (RO)-based desalination technology is in place at the pilot study stage in numerous coastal communities. The photovoltaics reverse osmosis system, in this regard, may have a positive effect on disaster risk reduction-based programs to provide coastal households with drinking water and growing resilience in water security-related matters. Nevertheless, the environmental impacts associated with desalination plants should be reviewed with very high emphasis.

In satisfying the increasing needs of water security in developing countries, as well as rural communities of coastal areas, one can use solar energy and photothermal seawater membranes [50–52]. This method of getting desalinated water will be economically feasible, fitting for decentralized coastal locations, easy to use with time variant flexibility, appropriate for potable water solutions that can reduce standard power requirements, as well as fulfilling the energy requirements [50].

## 4. Conclusion

In the realms of the energy-water nexus, wastewater remediation technologies systems should be planned carefully to overcome serious errors in the choice of WWT methods. To accomplish water security, we need to move our conventional water utilization to unconventional water sources, such as industrial greywater, wastewater, brackish groundwater, seawater, and storm water. To achieve the Sustainable Development Goals, we need to consider energy sources that are less carbon-emitting as well as zero liquid discharge water to tackle climate change and environmental/industrial pollution. New emerging technologies can be the answer to achieve water security and Sustainable Development Goal targets. However, we should always remember that advanced technologies should be greener and environmentally friendly. Discharging pollutants from the treatment plants may subsequently put a strain on the coastal and marine biological-ecosystems as well as the vulnerable

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mangrove ecosystems, if present. Moreover, among the numerous advanced techniques, the thermal desalination/RO techniques are the most energy-intensive, with large carbon footprints, and not sustainable for the water-energy nexus to achieve water security. Although membrane-based desalination is growing fast, membrane fouling still poses a serious problem. Another serious problem is generation of end-of-life solid membrane wastes, which usually go to landfill, as well as possessing an enormous carbon footprint.

The major hindrances of desalination plants make them vastly expensive in terms of the water-energy nexus and certainly not justifiable strategically in many energy- and water-starved parts of the world. Choosing the right type of technology should be strategically planned, designed, and implemented to attain water security. Although the fresh water demand market is steadily growing around the globe, based on membrane-based RO processes, integration of renewable energy such as photovoltaics (PVs)-reverse osmosis (RO), developing nanomaterial for energy efficient membranes, forward osmosis, and hybridization of different techniques can lessen the carbon footprint and enhance the cost effectiveness as well as increase water security.

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CHAPTER

# 6 Bioelectrochemical systems: Understanding the basics and overcoming the challenges

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## 1. Introduction

In bioengineering technology, bioelectrochemical system (BES) is a new area of interest that makes use of microorganisms and enzymes along with the electrochemical method and in turn enhances the oxidation-reduction mechanism. Basically, the process involved in BES show the generation of the electron power. It also reaches the goal of reduction reaction taking place successfully that has been hindered by the electron donors and electron acceptors [1]. The key areas in the challenges for researchers include optimization and selection of materials used in electrode, sorting of electrochemically active and inactive model microorganisms, and finally designing the electrochemical devices. Earlier these systems were applied in fabricating microbial fuel cells (MFC) when M. Potter [2] showed the studies of the electric current generation by several microorganisms, which convert chemical energy into electrical energy by degradation of various substrates, mostly the organic moieties from water effluents [3]. The rise in the population growth also demands maintenance of high economic growth that in turn continually fuels the pollution in the environment and also creating ever-growing need for energy resources. In recent years, the idea of utilizing waste materials as a potential source for harvesting energy has come up. This exploits the methodology of electrochemical conversion of organic matter to frame reusable fuels, by-products, and electricity by microbial conversion involving metabolites. Moreover 80% of global energy production employed as a main energy source of fossil fuels. This is due to their high-energy efficiency and affordability. Though these are massively used, they are prone to cause excessive emissions of greenhouse gases beyond the capacity of earth to eliminate it. This favors the climatic changes induced global warming and hence there are concerns highlighted by researchers in the field to explore and analyze the alternative resources of energy for attaining sustainability.



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Among the widely trending and acceptable technologies, fuels cells are considered to be one of the conversion systems that generates electricity without releasing greenhouse gases (GHGs) from fuels such as hydrogen and alcohols. Proton-exchange membrane fuel cells (PEMFCs) consists of two electrodes with proton exchange membrane between them. Catalysts at anode promote oxidation of hydrogen along with electrons and protons release and travel toward cathode for producing water. PEMFCs have been widely explored, and different noble metals have also been implemented as catalysts at anode and cathode for redox reaction at higher reaction rate.

Though all the processes in PEMFC include no emissions of GHGs, it should not be missed that the methods currently in use for hydrogen generation does release $CO_2$ and consumes heat via combustion, water-gas shift reaction, and steam-reforming reactions at high temperature. In addition, cryogenic storage material and compressor are mandatory due to the volume expansion of the hydrogen in gas phase at ambient pressure and temperature. These properties may lead to explosion and requires huge storage space.

On contrary, MFC is a BESs that can generate electricity by bacterial interactions occurring at anode. In this context, various BESs have come up suggesting wide applications for chemical synthesis and renewable energy production. From all the previous investigations, scientific progress for understanding the mechanism and development of efficient materials have been made. There are vivid types of BES, and immense work has been published to draw attention on various aspects of BES such as design components, microbes' selection, electrode material and catalyst, pollutant removal, substrates, and modeling aspects so that its performance is enhanced.

However, there exist very less data regarding the economic assessment of different types of BESs that is crucial to broadly persuade the significance and economic viability of BESs in circular bioeconomic model to our societies. Technological analysis of BES is currently at a growing stage, and it is advisable to have a summary and detailed review for the economic feasibility. Considering these research gaps, this book chapter depicts the basic understanding of BES and its scaling up hurdles along with its drawbacks. Various types of BES are described, and the advantages toward bioenergy recovery have been noted. Efforts for making this technology worthwhile for field application are going simultaneously [4]. Considering BESs as a part of circular bioeconomy, principles of BES would be introduced before economic viability studies. Current challenges and future pathways for research are also stated in this chapter.

## 2. BES and its classification

Like other types of electrochemical cells (e.g., batteries), both membrane fuel cells (MFCs) and microbial electrolysis cells (MECs) consist of two electrodes (i.e., an anode and a cathode) that are connected with a conductive wire to form a closed electrical circuit [5]. Fig. 6.1 shows the schematic representation of basic fuel cell.

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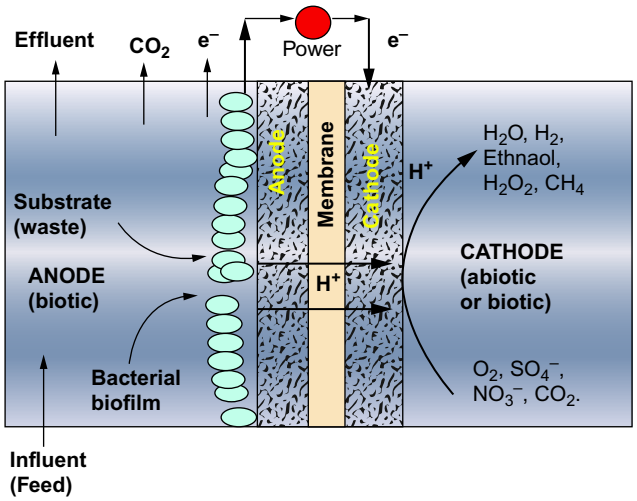


**FIG. 6.1**

Schematic representation of fuel cell.

The biological and electrochemical processes in both types of BESs are uniquely linked by the electron exchange between the microorganisms and electrodes. The electrons can be transferred (1) directly, via the outer membrane proteins (e.g., cytochromes) or conductive nanowires of the microorganisms or (2) indirectly, through electron shuttles (e.g., flavins), when there is no physical interaction between the electrodes and microorganisms [3]. On the cathode side, the transferred electrons can be utilized to accomplish any reduction reactions, which lead to diverse application possibilities of BES [6].

## 2.1 Principle and thermodynamics of BES

The basic motto of the BES works on the electrochemical conversion where chemical energy from the biodegradable organics is converted to electrical by catalytic activity of microbes. Proton exchange membrane (PEM) separates anodic and cathodic half-cell causing reduction and oxidation reactions. The bacteria which are electrochemically active catalyzes the electron donors and deliver toward anode. These electrons can be directly seized for bioelectricity by exporting them to external circuit. Protons travel from anodic to cathodic chamber to maintain electroneutrality. Here, both protons and electrons gets utilized in the reactions occurring at cathode. Significant attraction has been gained by BES due to its various applications in scientific fields like bioremediation, wastewater treatment, and producing renewable energy. There are five variants in BESs, which are shown in tabular format in Fig. 6.2.

In MFC, oxidation of $e^-$ donor for, e.g., acetate is coupled with $e^-$ acceptor like oxygen at the cathode. So, acetate would be oxidized to $HCO_3^-$ at electrode potential

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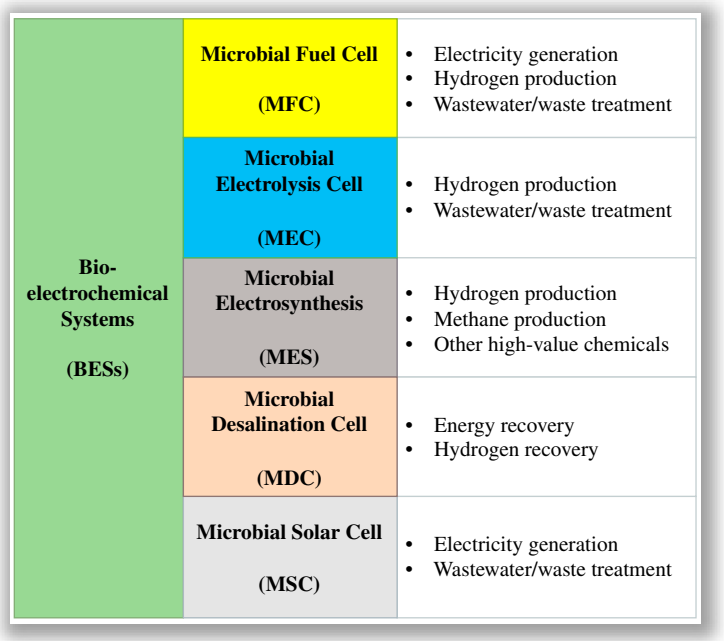


**FIG. 6.2**

Various types of bioelectrochemical systems and their application.

of −0.28 V vs standard hydrogen electrode (SHE) and oxygen is reduced to water at a potential of 0.82 V vs SHE. The resulting voltage (in this case 1.10 V) is positive and thus generates power. While in MEC, oxygen is absent at cathode and thus other acceptors get reduced like $H^+$ to $H_2$ which occurs at a potential of −0.41 V vs SHE. The resulting cell voltage is (−0.13) which favors the nonspontaneous reaction and in turn requires external source of energy to accelerate the reaction [7,8].

BES can be operated similarly to MFC or MEC; where electric power is recovered or external power is recovered respectively to enhance the kinetics of reaction. Due to these losses in the system, energy gained is quite less and the required energy is quite higher than calculated value. There are some losses due to imperfect catalysis called activation overpotential losses, while resistance in electrolyte and electrode causes ohmic loss. Some concentration losses occur due to substrate diffusion to the anode oxygen at cathode [9].

## 2.2 Microbial ES

Microbial electrochemical system can be divided into MFC and MEC depending on their electron transfer and the reaction type. MFCs that possess an electrochemical system with microbes as a biocatalyst in an anodic chamber are widely utilized for generating electricity by different substrates. In MFCs, electrons released from the

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intracellular metabolism shift to anode and finally captured by cathode via external circuit for reducing electron acceptor and oxygen by generating current [10]. Many reports have been published on MFCs that act as an innovative wastewater mechanism for eliminating pollution and generating energy. Though BES has been successfully applied in MFCs by utilizing varied microorganisms that produce power density ranging from 3800 to 4000 $mW/m^2$, the high material costs and mediocre power generation are still considered as major drawbacks to take this applications further on a large scale. Some electrodes raise the cost as they are equipped with gold, platinum, and few others adopt bacteria as catalysts. Thus, the biofilm forms on anodic electrode surface that strengthens the electron transfer. Hence, the practical uses of MFCs are confined to microorganisms since stabilities and efficiencies of microbial reactions depend on the external environment that differs from the original environment such high toxicity, low temperature, and high salinity. Internal resistance of the cell is also another drawback that is caused by PEM resulting into low-power density and low current density [11].

MECs are modified MFCs where bacteria called exoelectrogens oxidizes a substrate and releases electrons toward anode. Usually in MFCs, oxidation takes place in anodic chamber and later is shifted to cathodic chamber. But in MECs, the potential poised at cathodic chamber is analyzed by bacteria and electron transports due to their differences in the potential. Moreover, due to the electron or loss of energy, the potential at the cathode does not equal to the theoretical potential difference of electron transports. There are few limitations of scaling up of MECs as most of the microbial electrosynthesis systems possess low production rates with low energy efficiencies. Another drawback for MECs include chemical incompatibleness between biotic and abiotic catalysis [10,12]. For example, toxicity is due to electrode leaching, and fouling of electrodes is due to microbes. MECs are also an effective method for hydrogen recovery from swine wastewater treatment, although the process needs to be further evaluated for reducing methane production. Abundant by-product of biodiesel production, i.e., glycerol has also been used as a substrate in MECs even though applied higher voltage (0.9 V) than the one of 0.5 V that being used for acetate. Still, it is a matter of investigation whether the electrons releasing from the cathode can be transferred between bacteria and cathode. To conclude in a line, these MFCs and MECs rely on the possibility of an electron transfer and rate of electron transfer between cells that are the key parameters for deterring the systems efficacy.

## 2.3 Enzymatic ES

This type of BES also makes use of a catalyst as the electron with the enzymes serve as the external electron donor or acceptor. Enzymatic electrochemical system has been widely accepted in study of in vitro electron transfer mechanism as the electron transfer kinetics is stipulated. Also, the oxidoreductase can be generated by releasing or capturing the electrons at the electrode's surface. Earlier reports have shown that these electrochemical methods have been applied to investigate the mechanisms of the electrons and ion transfer in in vivo conditions. High sensitivity and high

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reliability make it easier to study the mechanism of enzyme reactions [13]. When NADH:Quinine complex I was fixed on surface of the gold-modified electrode, the process of electron and proton transfer effectively reoccurred in in vivo with electrode sole acceptor. High surface area materials were incorporated in this system with high density to increase the load of enzyme for higher catalytic rate [14].

Though all these electrochemical systems are being utilized since decades, devices with electrochemical upgradation and novel biocompatible materials of electrode are always commanding. Yet, the mechanisms of the energy output and electron transfer are still in stage of infancy [15,16].

## 3. Necessity and working of BES

If we see globally, billions of euros are spent to treat trillion liters of wastewater each year that consumes extensive amount of energy. This wastewater can do wonders as a potential renewable resource that would save major amount of money and energy because it comprises of the organic pollutants that can be further utilized to generate electricity, high-value chemicals (caustic soda), and hydrogen. All this can be attained if the electrically active bacteria breakdown the organic matter in the electrochemical cell that simultaneously cleans up the wastewater. We can recover energy from wastewater, we can also treat wastewater without using extra energy, can produce hydrogen from it, and thus safeguard the cost-effective production of valuable chemicals [17].

MFCs and MECs are two rapidly flourishing biotechnologies that combine electrical and biological processes. Fig. 6.3 shows the example of wastewater by MFCs and MECs through schematic diagram. These are the type of batteries termed as electrochemical cells consisting of two electrodes; anode and a cathode. An external wire is joined to it for completing the electrical circuit. Basically, MFCs are fabricated to produce electricity and MECs utilize this electricity to drive the chemical reactions occurring at cathode to produce hydrogen or other chemicals. Both MFCs and MECs can achieve this by removing the organic matter and treating wastewater. In these, there are special kind of microorganisms, mainly bacteria that is present in wastewater and can break down the organic materials found at anode under anaerobic conditions. During the breaking process, the bacteria gives out carbon dioxide, electrons, and protons into the solution. Electrons are collected at anode that further travels via external circuit to the cathode. Protons travel through the solution in the cell toward cathode thus capturing and reusing the carbon dioxide. Talking about MFC, extraction of electron carrying external circuit leads to electricity production. Under aerobic conditions, electrons arrive at the cathode. This means that it combines with the oxygen and protons in the presence of air to form water. While MEC is a type of modified MFC. If oxygen is excluded from cathode, electrons that are being released during breaking of the organic matter can combine with protons to produce hydrogen. This is not a quick reaction, and little amount of external energy is required to be added to the system to drive the whole process. These are also commercially set up to gain value-added products like caustic soda [18].

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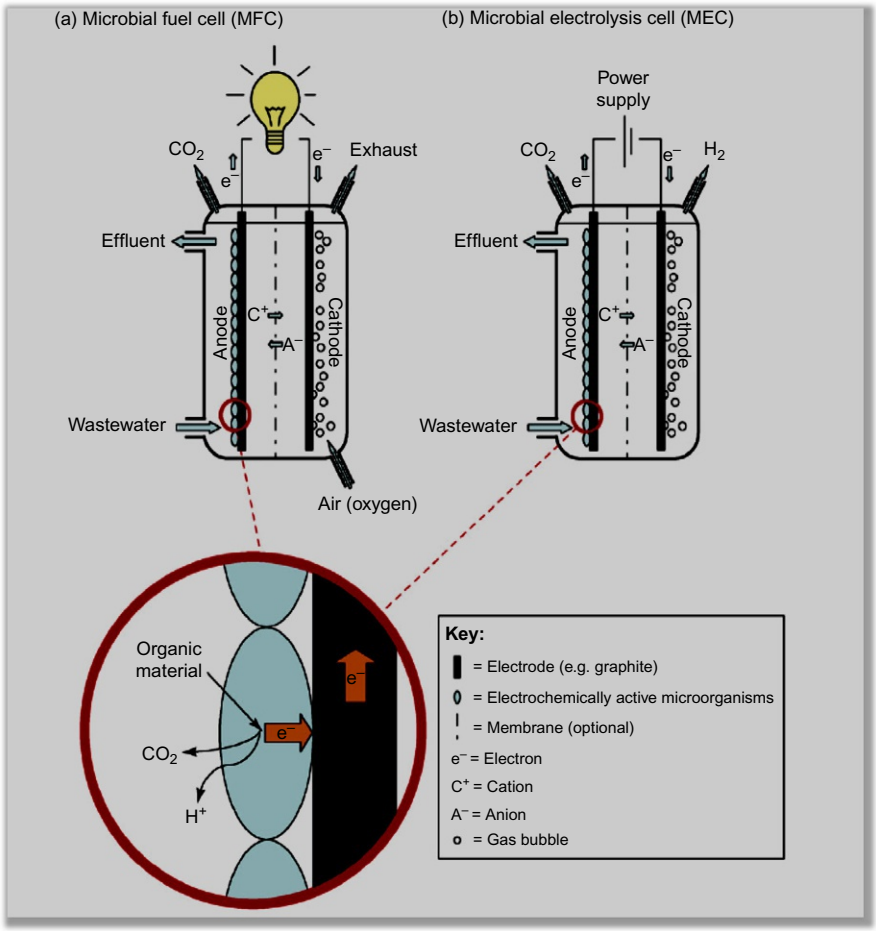


**FIG. 6.3**

Schematic representation of two common bioelectrochemical systems example for wastewater (A) microbial fuel cell (B) microbial electrolysis cell.

# 4. Types of electron transfer in BES

## 4.1 Extracellular

As we are aware that microbes act as a catalyst in MFCs and MECs while enzymes in the enzymatic electrochemical system. There exists a small molecule having capability to undergo redox cycling (electron shuttle), which serves as a terminal electron acceptor. Once it gets reduced, it can itself transfer $e^-$ to iron oxides and become reoxidized. This shuttle creates a basis for indirect reduction process. Thus, mainly a molecule with single shuttle can recycle loads of times that can result into the significant effect on terminal oxidant for turnover in the given environment. Organic

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compounds like humic substances, thiol compounds, phenazines, and quinones are some of the examples that can play this role, but any substance reversibly redox active possessing the redox potential can be useful. In MECs, given voltage poises at cathode electrode, and the electrons from the intracellular reduction and energy mechanism are captured by strains after releasing from cathode. Due to the insulation of the cell membrane, electrons can smoothly swim across the membrane. As there exist different mechanisms of the electron transfer, three major mechanisms between electrodes and microorganisms exist. They mostly rely on the nanowire, outer membrane protein and are mediated by endogenous and exogenous electron shuttles. Overall, we classify the shuttles according to their presence in the environment (exogenous) or their cell production (endogenous). The strains that are electrochemically active evolve different conductive methodology. *Shewanella* has a complete set of extracellular electron transport chain. The electron transport channels that were formed by outer membrane mediate the directly electron transfer between cells and Meanwhile, the synthesis and release of riboflavin assist electron transmembrane transfer, but this process requires specific transport system [19]. Another model electrochemical active strain, *Geobacter*, can synthesize conductive pili (nanowires) through cell growth and involve in directly extracellular electron transfer between cell and electrodes [20]. Also, outer membrane cytochrome is necessary for electron capturing [5].

## 4.2 Intracellular

Series of electron and proton along with the coenzyme Q, cytochrome, and oxidoreductases constitute the electron transfer chain (ETC) also called as respiratory chain in this intracellular type of BES. The main motto of the electron shuttle, nanowire, and modified electrode is to enhance the cells interaction with electrodes. Within this ETC, electron transfer takes place from high potential $e^-$ donor to low potential $e^-$ acceptor with the synthesis of ATP. Cytochrome anchored at membrane could enable the intracellular metabolism and transfer of electron for the electrochemical bacteria. *Shewanella* and *Geobacter* are electrochemically active bacteria having excellent ability of electron transfer and hence widely used in MFCs. Previous literature reports depict that few strains can alter the electron transfer route based on the potential differences of available electron acceptors and donors. While *Shewanella* can gain bidirectional $e^-$ transfer with only one intracellular $e^-$ transfer system in MECs and MFCs. Electron mediator used is the only difference. In comparison with *Shewanella*, three electron leaking mechanism persist in *Geobacter* ehichinclude; OmcE/OmcS used for Fe (III) reduction, electron transfer OmcZ between cells, and nanowire used for electrode interactions [21].

Electrochemical bacteria that is inactive can interact with electrode in the existence of electron shuttles. Electron shuttles that are bio-based, such as riboflavin, coenzyme Q, or its analogue, can assimilate into essential ETC directly via diffusion or membrane transporter and contribute in intracellular reduction and energy metabolism. Compared to bio-based electron shuttles, chemical-based electron shuttles

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have faster diffusion rate and its high polarization characteristics safeguard effective bidirectional transportation across the membrane. However, the relation between intracellular ETC and the chemical-based electron shuttles is still not flawless. Some studies showed that neutral red can participate into membrane and perform the function of native electron transfer mediators [22]. Till date, its assured that, even if the mechanism is not clear, $e^-$ shuttles can capture or release electron between intracellular ETC and electrode. Electron transferring efficiency of intracellular ETC as compared to the active electrochemical strains is not effective. Hence, metabolic engineering policies have been useful to rebuild the intracellular ETC for encouraging electron transfer in an electrochemical inactive bacteria. Sturm et al. found that heterologous expression of intracellular ETC from *Shewanella* (CymA, Mtr system) in *E. coli* could reprogram intracellular metabolism and quicken the intracellular electron transfer rate by 183% [23]. In addition, higher electricity power output was attained with the help of methylene blue.

# 5. Applications of BES

## 5.1 Recovery of nutrients

Nutrient removal and recovery have been gaining less consideration during the growth of BES for energy-efficient treatment of wastewater, but, still it is a serious issue for sustainable wastewater treatment. Both nitrogen and phosphorus can be removed and recovered in a BES through a method that involves biological processes such as nitrification and bioelectrochemical denitrification, the couple ($NH_4^+/NH_3$) affected by the pH of electrolyte, or precipitating phosphorus compounds in the high pH region together in a cathode electrode. Thus, reports show that BES has been useful in the nutrients removal and recovery in various types of BES including MFCs and microbial electrolysis cells. This has brought instructive outline of the current development and has inspired to think more and investigate towards further development of efficient processes for removal and recovery of nutrients in a BES. Incorporating nutrients removal/recovery into a BES would make it beneficial over the existing technologies, and the literature demonstrates the viability of nutrient removal/recovery at a bench scale. This is a stimulating subject in BES development, which needs to be investigated more to point out some of the key challenges, especially at the level of efficient demonstration and evolution. Nutrient removal/recovery should be niche-based application, i.e., depending on the precise circumstances such as wastewater features and the main purpose of BES [18].

## 5.2 Valorizing carbon dioxide

The swift expansion of a wide range of industrial skills using fossil fuel has led to significant increase in the level of atmospheric carbon dioxide ($CO_2$). Also, a massive number of reports confirm that preeminent carbon dioxide level in the atmosphere can be a decisive factor of global warming via greenhouse effects. The

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conversion of $CO_2$ to value-added chemicals has been theorized as a vital technology to slug down the rate of atmospheric ($CO_2$) accumulation. Fortunately, $CO_2$ is an encouraging renewable source to produce ecological friendly chemical platforms such as formate, dimethyl carbonate, its polymers, and others [24]. Usually, the organic substrates devised from sugars are utilized as an organic feedstock for the bioproduction of chemicals and fuels because they are already partially reduced and have been associated with the requirement of lower reduction power demand for the bioproduction process. Nevertheless, to refine the substrate to its pure form and utilize it as a starting material in bioproduction can be expensive. Moreover, sugar-based substrates for bioproduction create undesirable intrusion with their other uses. On the other hand, organic wastes having low utility value such as fatty acids, glycerol, and carbon dioxide in the perspective of the recent development in MES have become hopeful substitutes for the cost-effective organics [25].

## 5.3 Valorizing contaminated water

Electrochemistry and biotechnology can treat wastewater by combining these two technologies into BES. This means, two sciences in the treatment of industrial wastewater are coupled via assimilating electrodes inside the biological reactor, to recover resources contained in wastewater.

BES technologies include integration of anode and cathode within the biological reactors. Thus, by the aid of microorganisms actually the organic materials that are adhered to the electrodes, the BES catalyzes different oxidation and reduction reactions to valorize the resources enclosed in the wastewater. The electrons that are obtained as a consequence from this oxidation are transported to the anode and further used to produce electrical energy [26].

## 5.4 Valorizing energy

The fabrication of renewable biomass often comprises generation of waste, by-products, and coproducts. In massive quantities, lignocellulosic biomass is accessible that provides an enormous potential for producing bioethanol. These both could potentially create a rich source of substrate to be utilized in BESs. Biomass is the fourth largest energy source after oil, natural gas, and coal, which is found commonly at a global scale. This is considered as the most important renewable energy option presently that can be altered in to different forms of energy [27]. Hence, it is proficient of providing all the energy facilities required in a modern society. One of the example of feedstock can be very helpful in BES. Additional cellulose fuel always exists in the form of crop residue discarded after the harvest, and its manure is abundant. Rumen contents, which generally are thrown away, are available each time when these ruminants (goats, llamas, sheep, cattle, and camels) are slaughtered.

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## 5.5 Product formation and recovery

It has been known for quite some time that BESs can have applications other than wastewater treatment and electric power generation. This field addresses the use of microorganisms as catalysts on cathodes (i.e., biocathodes) to achieve electricity-driven synthesis of chemicals and fuels. Some of the products that have been explored in BES are described below:

### 5.5.1 Hydrogen peroxide

The manufacture of hydrogen peroxide ($H_2O_2$), which is a crucial industrial chemical in BES, was reported at an anode coupled to the cathodic reduction of oxygen to $H_2O_2$ based on the bioelectrochemical oxidation of organic wastewater [28]. When the applied voltage was 0.5 V, the system was able to produce approximately 1.9 kg $H_2O_2/m^3$/day from acetate with 83.1% overall efficiency. Besides the aforementioned applications of BESs as a tool for bioremediation and product synthesis, they can also be applied into biosensors. Several researchers have reported the advancement of BES-based biosensors in past few decades [29,30].

### 5.5.2 Methane

The making of methane in the cathode of an MEC in earlier times was considered as an irritation, and it is just recently that electrochemical production of methane at cathode of a MEC is being considered as a striking option [31]. The conversion of acetate to hydrogen is thermodynamically adverse under standard conditions (+13.8 kJ $mol^{-1}$ electrons or 0.48 kWh $kg^{-1}$ COD) and thus additional voltage of at least 0.14 V needs to be applied to the MEC. In practice, minimum 0.2 V needs to be applied to commence the current generation. Provided that the electron donor is "free" from organic compounds, and the applied electrical energy is less than the specific energy content of the end product, thus positive energy balance can theoretically be obtained in a MEC [32].

### 5.5.3 Ethanol

Biological acetate reduction with hydrogen is a potential method to transform dank biomass waste into ethanol. Recently, the ethanol from acetate reduction via methyl viologen (MV) as mediator in the cathode box of a BES was established. Ethanol production showed a CE of 49% [33]. Besides this, *n*-butyrate, hydrogen, *n*-butyrate, ethanol, and the nonreversible reduced $MV^{2+}$ were formed in the cathode. MV withdrew the side reaction of methanogenesis and also improved ethanol production. However, it was worn-out rapidly owing to irreversible reduction at the cathode, and in its absence, high yields of an undesired end product (butyrate) were found followed by commencement of methanogenesis [34,35].

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## 5.6 Recalcitrant pollutant degradation

Besides hydrogen production in MECs and electric power generation in MFCs, theses BESs have also been useful to treat specific recalcitrant pollutants. These include industrial wastewaters from municipal, food, paper, and breweries. Some examples are described below.

### 5.6.1 Sulfide removal

Apart from organics, wastewaters often contain inorganic matters, such as sulfide. This is a hazardous substance that needs to be eliminated from wastewater before discharging into the environment. Sulfides role is to be a mobile carrier of electrons from bacteria to electron acceptors such as Fe(III) (hydr)oxides. The multivalency of sulfur coupled with their facile interconversion and the diversity of sulfur compounds have made oxidation of sulfide in MFCs very intricate. The MFC system has been found to be effective for sulfide removal and generation of electricity simultaneously. The oxidation of sulfide in the anodic compartment resulted in electricity generation with power outputs up to $47\,W\,m^{-3}$ [36]. Also by regulating the anode potential, the corresponding efflux of sulfide was reduced. Later it also portrayed that the microbe-assisted sulfide oxidation produced a higher persistent density of current than the sulfide oxidation via only single electrochemical reaction [37].

### 5.6.2 Dye removal

Dyes are widely used in different industries, especially in the textile manufacturing. The treatment of effluents containing dyes is indispensable due to their toxicity, carcinogenic impact, and pollution effect on environment [38]. In recent years, several studies have focused on the treatment of dye containing wastewaters in the BESs. Simultaneous azo dye degradation and bioelectricity generation utilizing a single chamber MFC have been investigated. Effective decolorization of a metal azo dye at the cathode of a BES was achieved while oxidizing acetate in the anode. Yet another study concentrated on reduction of azo dyes in cathode of the MFC harnessing electrons produced from metabolic oxidation of *Klebsiella pneumoniae* strain L17 in the anode [39]. Similarly, MFC systems have been used for the decolorization of Congo red by providing various cosubstrates such as acetate. MFCs operated at higher power densities could simultaneously increase COD removal efficiency as well as the rate of dye decolorization, even though bioelectricity generation seemed to be competitive to dye decolorization [40,41].

### 5.6.3 Leachate treatment

Leachates are expulsions from landfills with high absorption of complex organic matters and ammonium-nitrogen, distinguishing it from municipal wastewater, which may cause some serious problems such as contaminations to ambient ground water, eutrophication of water bodies, or odor release. The main problem with leachate treatment is that the ammonium concentrations at these levels persist for many years after a landfill has been closed and levels of other pollutants, such as COD and biological oxygen demand (BOD), have dropped [42]. Leachate is considered a well

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matched substrate for use in an MFC because of its relatively high amount of organics, conductivity, and buffering capacity, yet minimal solids. The greater power density obtained in one of the studies can be attributed to the smaller scale MFC and the modified leachate substrate [33,43].

#### 5.6.4 Organochlorine removal

Chlorinated aliphatic hydrocarbons (CAH) rather chlorinated solvents like 1,2-dichloroethane (1,2-DCA) and trichloroethylene (TCE) are used in industries as major solvents and also as degreasing agents that enter and pollute the soil and groundwater via leakage through storage tanks along with poor storage and disposal practices. Recently, BESs have been proposed in which the solid-state electrodes (e.g., graphite) are employed as direct electron donors by replacing organic electron donors in the reductive dechlorination. Progress of bioelectrochemical remediation technologies for TCE has discovered that specific dechlorinating bacteria are able to "pick" electrons from the surface of potentiostatically controlled electrodes and applying them metabolically for reducing CAHs. The reduction current subsequently obtained from the reductive microbial dechlorination can be continuously measured with a potentiostat [33,44].

## 6. Factors affecting BES

### 6.1 Effect of type of electrode

To reduce the cost of the reactors and enhance the performance of MECs and MFCs, numerous types of electrodes have been developed and investigated. The electrodes not only act as conductors in BESs but also habitat as electrogenic microbes. Hence, best electrode materials should depict peculiar surface characteristics such as ability to transfer electrons between microbes and electrodes, high specific surface area, biocompatibility, and considerable roughness [45]. Owing to these characteristics, carbonaceous materials are used as anode materials (e.g., carbon paper, graphitic brush, and carbon cloth). When carbon paper was used as electrodes, the performance was found to be slightly better than graphitic brush. The high specific surface areas of carbon cloth and carbon paper are believed to be the vital factors to their greater power generation and removal of COD [46].

### 6.2 Effect of different substrate

The appropriateness of wastewater sources for MFCs and MECs mainly depends on the biodegradability of the containing substrates, but other characteristics of the wastewater, such as pH, ionic strength, and toxicity, would also make a difference. Landfill leachate, domestic water, and swine water are three major wastewater resources used to feed MECs and MFCs. By generation of power in MFCs and hydrogen production, treatment methodologies are statistically analyzed and compared [47,63]. Though biodegradable organics constitute swine water and landfill leachate,

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that have high ionic strengths, the relatively high concentrations of toxic compounds like ammonium and heavy metals would negatively affect the microbial growth and slowly the reactor performance [48].

## 6.3 Effect of reactor type

The configuration of reactor plays an important role in the performance of MFCs and MECs. Studies were carried for single- and two-chamber design by Logan B.E [49]. The results inferred that the two-chamber MFCs were able to generate high power, while the one-chamber MECs could produce biohydrogen in greater amount. However, the two-chamber systems seemed to be tricky with high electrical resistivity that should give relatively lower power generation in MFCs than the single-chamber designs. In fact, two-chamber systems were more often used in existing analysis due to their simplicity and stability. A great variety of substrates and operating conditions have been investigated using two-chamber systems, and mostly the substrates were readily biodegradable (e.g., acetate) for which conditions were found optimal [50–52].

## 6.4 Effect of pH

The anode pH also greatly affects the performance of MFCs and MECs. A pH between 6.5 and 7.5 correlates with relatively higher power densities, up to over 1200 $mW/m^2$, whereas a pH between 5 and 6 derives a more significant hydrogen production rate, as high as about 8 $m^3$ $H_2/m^3/d$. The impacts of pH on the CO removal in both types of reactors are also pronounced. The COD removal at the optimal pH ranges is nearly three times higher than that at extremely low or high pH ranges. These results reflect that the microbial activities in MFCs and MECs are slower at suboptimal pH than at the optimal pH [53,62]. The low values for both power generation MFCs and hydrogen production in MECs at high pH ($>10$) might be due to the poor proton transfer, as the proton concentration gradient across the PEM decreased. Proton transfer is known as a rate-limiting factor for both types of reactors. The reports state that, in comparison to MFCs, MECs due to the absence of production of biohydrogen in cathode chamber are more vulnerable to pH [54].

## 6.5 Effect of temperature

Like many other anaerobic reactors, MFCs and MECs are sensitive to temperature. The power generation in MFCs and the hydrogen production in MECs, as well as the COD removal in both types of reactors, vary drastically as the working temperature changes. In general, temperatures that are either too high (e.g., $>45°C$) or too low (e.g., $<15°C$) significantly hinder power generation in MFCs and hydrogen production in MECs, while temperatures between 30°C and 40°C seem to favor the performance of these reactors. At the same time, the highest COD removal in both MFCs and MECs has been found within the temperature range from 25°C to 35°C. In terms

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of the principle of economy, Tang et al. suggested the optimal operating temperature of MFC be 30°C, even though the performance at 35°C slightly improved [55,56].

### 6.6 Effect of external resistance

External resistance ($R_{ext}$) affects the performance of MFCs and MECs, by limiting the flow of electrons form the anode to the cathode. According to Ohm's Law ($V = I R_{ext}$), both the potential ($V$) and the current ($I$) outputs would be influenced. Consequently, the power output ($W$) is also affected as shown by $W = I^2 R_{ext}$. In MFCs and MECs, increased external resistance decreases the power density, as well as the treatment efficiency [57]. Generally, the anode potential, which directly determines the anode availability as electron acceptors, is regulated by the external resistance [58].

## 7. Shortcomings of BES

Though substantial progress has been done to improve the performance of BES in the last few decades, still, it surfaces many challenges toward commercialization like expensive electrode accessories, low-power output, proper scaling up, and costly separators. Microbial fuel cells usually work as a source of voltage with an internal resistance. The power generation in MFC is of high order of magnitude and less than that obtained in chemical fuel cells. As soon as the current begins to flow through an external circuit, the voltage drops due to different losses which in turn decreases the actual cell potential and not the theoretical potential. These losses are stated as the activation loss ($\eta_{act}$), the concentration loss ($\eta_{conc}$), Coulombic losses, and ohmic losses ($\eta_{ohm}$). The activation loss is because of the activation energy needed to undergo reactions at each electrode, concentration loss is due to reduction of reactants at electrodes, and Ohmic losses are due to the electronic flow through the electrodes, the current collectors, and the contacts, the external resistance as well as the ionic flow through the electrolyte. Coulombic loss occurs as a reason of parasitic reactions that do not contribute to current generation [32,59].

Researchers have reported maximum power of 2.15 kW/m$^3$ from 0.335 mL and 1.55 kW/m$^3$ from 2.5 mL of anodic chamber volume of MFC. Yet scaling up remains a crucial challenge related to BES. Most of the studies of BES have been taking place in anodic chamber at lab scales volume ranging from few mL to L [60].

In order to make MFCs appropriate for practical applications, such as wastewater treatment plants, it is significant to achieve high-power densities at a large scale. Apart from that, the MFCs are having a potential for wastewater treatment and energy recovery; limited studies have been reported on scaling up so far. All this describes that it is needed to improve the power output of this device by using cost-effective materials, specially developing low-cost electrode catalyst materials that can support very high current densities (greater than 5 A/m$^2$), for its fabrication and need to come up with advanced design to minimize losses and support higher volume of anodic chamber beneficial in large-scale applications [61].

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## 8. Conclusion and future prospects

Expansion of MFCs to generate electricity has opened the gateways for future applications of BES that transforms the way wastewater is treated. It has also altered the methods of production for other numerous chemicals, such as caustic soda, bioplastics, and hydrogen peroxide. The technology is likely to evolve as a way of treating sewage, industrial, or agricultural wastewater, by not only lowering the amount of energy needed, but, at the same time, producing electricity, hydrogen, or other chemicals of high value. Wastewater, when used in this way, provides both energy-saving benefits and high-value products and can be regarded as a resource rather than a problem requiring costly treatment.

Presently, electricity is not considered valuable enough as an end-product to justify the cost of producing it utilizing a BES system, i.e., the costs of the wires and collectors outweigh the value of electricity produced. However, chemicals, such as caustic soda, are more valuable, and the economic case for chemical production is stronger, especially if such products are produced and used locally. To sum up, it is evident that BES technology, mainly in the subject of biological research, is varying quickly, but several challenges remain for which it could take 2–5 years before first-generation technologies are available commercially.

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CHAPTER

# 7 Emerging trends of cyanobacteria-based microbial fuel cells as an alternative energy source

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## 1. Introduction

### 1.1 World energy crisis

Energy is one of the key factors of human survival on earth. Increasing demand with the exponentially growing world population and depleting resources with excess usage following the modern industrial revolution have directed scientists' interest to search for alternative fuels [1]. According to the British Petroleum statistical review of world energy [2], global energy consumption mainly depends on fossil fuels consisting of 34% crude oil, 28% coal, and 23% natural gas. Other energy sources with special emphasis on hydro and nuclear are comparatively underused, contributing only 7% and 4%, respectively. Other renewables like wind power, solar gas, and biofuels represent a tiny contribution that accounts for less than 4% of world energy. It is common knowledge that fossil fuels are in a depleting spiral due to their excessive usage in the industrial sector, transport, other domestic uses, etc. As a result, researchers are endeavoring to find alternative and renewable energy sources [3]. An ideal fuel source should be environmentally friendly with low carbon emissions to ensure a sustainable future with low pollution. Various alternative energy sources such as geothermal energy, solar, wave energy, wind, and biofuels are commonplace, whereas biofuels (including solid, liquid and gas fuels) are one of the best alternatives in terms of usage and production process [1,3,4].

### 1.2 Most common alternative energies

Most countries are trying to fulfil their energy requirements through renewable energy technologies, including wind, marine, solar energy, and geothermal [5]. Most renewable energies are mainly facilitated by sources, which are naturally replenished



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with time. Sometimes it is challenging to distinguish renewable and nonrenewable energies separately, and bio-derived alternative energy types such as biodiesel, bioethanol, biomass, and biogas by anaerobic microbial breakdown are widely considered renewable energies. Solar light is the most available renewable electricity source on the earth, which is not fully used to date. It is a tangible solution for powering scale [6], and most importantly, there is no need for high transportation costs. For example, photovoltaic cells empower small electrical devices by a current generation with the availability of solar light. However, the solar cell implementation costs are high at first, and its environmental impact should be a concern [6]. Wind energy is considered to have a high potential to be transformed into electricity and mechanical power and is highly dependent on location [7]. Hydroelectric power is known as "hydropower" which converts flowing water kinetic energy to electricity through a turbine. According to International Renewable Agency [8], this is one of the oldest power generation mechanisms and still plays a significant role in world electricity generation (around 16.5% of the total electricity generation). Tidal power is also considered a type of hydropower that converts tidal kinetic energy to electricity. Though tides are more easily predictable than other energy sources such as solar light and wind, higher production costs and the higher modern construction technology limit the tidal energy utilization in developed countries. Most renewable energies have common drawbacks such as high construction costs, location limitations, maintenance difficulties, and low output compared to existing operational existing energy sources [4].

### 1.2.1 Biofuel as alternative energy

Biofuel is the most promising alternative for fossil fuels that ensures environmental and economic sustainability [1].

Fossil fuels play a crucial part in the human lifestyle and accounts for 70% of the total global energy demand. Considering the trend of the future energy demand, sufficient supply, and environmental sustainability, biofuel is expected to replace fossil fuel [3,9]. However, conventional biofuel production from terrestrial crops can have a considerable influence on world food security [4]. Many studies on microalgae and cyanobacteria show potential in producing various types of third-generation biofuels [3,9]. Due to the culturing ability, higher growth rate, higher lipid accumulation, consumption of atmospheric $CO_2$, microalgae, and cyanobacteria are considered and highly considered for biofuel production [1,3,4]. Microalgae and cyanobacterial biofuels include biomethane, bioethanol [10], biodiesel [1,3], and biohydrogen [9].

### 1.2.2 Types of biofuels

Biofuels are found in solid, liquid, or gaseous fuels derived from organic matter (biomass). They are usually divided into two subcategories primary and secondary. Biofuels that are used in a simple form are called primary biofuels that are primarily used in household activities such as heating, cooking, or small-scale electricity production. With reference to the biomass type, the secondary biofuels are classified into first-, second-, third-, and fourth-generation biofuels. The first-generation biofuels

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are synthesized from edible feedstock such as corn, rapeseed, sugarcane, and soybean, whereas the second-generation biofuels are derived from nonedible feedstocks; *Jatropha,* switchgrass, corn cobs, animal waste, paper waste, food waste, etc. [1,9]. Based on the context of "Food vs Energy," the first-generation fuels are considered less sustainable with the fuel demand and food crisis. Furthermore, first- and second-generation biofuels are considered less sustainable due to the limited availability of cultivable land for edible and nonedible feedstocks [9], except for the waste products. The waste products such as cooking waste oil and paper waste have a higher potential for biodiesel and bioethanol production.

The biofuels belonging to the third generation are derived from microalgae and cyanobacteria (blue-green algae), and the metabolic engineering of photosynthetic organisms-based biofuel production belongs to fourth-generation biofuels [11]. Considering the land availability for plantation or culture, the harvest per hectare of microalgae and cyanobacteria is greater than the first- and second-generation plants as they can be cultured three-dimensionally [3,4].

### 1.2.3 Microalgae and cyanobacteria for energy production

Microalgae and cyanobacteria are the main concerns in third-generation biofuel production. They entail unique characteristics for sustainable fuel generation in the future. Microalgae and cyanobacteria are mainly sunlight-driven organisms, which are used to produce a wide range of bioactive compounds that include vitamins, pigments, carotenoids, ketones, and lipids, etc., and are useful as feedstocks for biofuels, foods, feeds, nitrogen-fixing biofertilizers, and in bioremediation applications [4,12]. Based on the advantages, algae biomass has more attention as a successful feedstock for alternative energy production. Moreover, there is no visible competition between algae biomass production with agricultural food and feed preparation despite limited arable lands for agriculture [13].

Cyanobacteria and microalgae are simple cellular photosynthetic organisms that are observed under the microscope and found in marine and freshwater environments. Cyanobacteria are photosynthetic prokaryotes with wide morphological diversity, with some members capable of fixing atmospheric $N_2$. They show higher photosynthesis ability and growth rates than other macroalgae and higher plants [1,14]. Microalgae are described as thallophytes that lack plant roots, stems, and leaves, and there is no sterile call covering the reproductive cells [15]. Unlike microalgae, cyanobacteria are a prominent phytoplankton group in eutrophic freshwater bodies. Cyanobacteria are morphologically diverse and are found as unicellular to small colonies of cells. The trichomes vary from simple to branched filamentous forms. Cyanobacteria are photosynthetic and contain only chlorophyll-$\alpha$ [12,14,16]. Cyanobacteria cultivation is comparatively easy and less expensive; therefore, cyanobacteria grow easily with only basic nutritional requirements (N and P). Furthermore, nitrogen-fixing strains can utilize atmospheric $N_2$ and $CO_2$ [12].

Microalgae and cyanobacteria have the intrinsic ability to produce 1 ton of algae biomass by consuming 1.83 tons of $CO_2$ in the atmosphere [17], and due to the simple

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structure and high cell surface/volume ratio, it leads to a higher rate of nutrient assimilation. Green algae growth is approximately 100 times greater than terrestrial plants, and most of the microalgal species double their biomass within 24 h and with 3.5 h of exponential growth phase [4,14].

Excess growth of algal blooms can adversely affect the aquatic environments and collapse the existing ecological equilibrium between other phytoplankton and other aquatic life forms. High densities of algal communities form an algal mat that covers the water surface and prevents sunlight penetration to the lower strata of water bodies. This can reduce the oxygen levels in water bodies and cause the death of aquatic flora and fauna due to hypoxia, or anoxic conditions which can adversely affect the environment, social activities, and the economy of the country. Subsequently, some bloom-forming cyanobacteria produce toxins as their secondary metabolites, namely hepatotoxins, cytotoxins, neurotoxins, and endotoxins [18]. These toxins can also affect human health following the consumption of water. Therefore, utilizing cyanobacteria or microalgae blooms for economically valuable processes have become important.

Due to the specific favorable properties of cyanobacteria, they are considered one of the most capable feedstocks for bioenergy production [3]. Recently, a bio-gaseous fuel, an algal-based biohydrogen, has been considered a successful alternative for electricity generation [9]. At the same time, microbial fuel cell (MFC) based technology had become a significant concern among scientists worldwide as an environmentally friendly alternative energy source with promising outcomes.

## 2. Microbial fuel cell (MFC) as an alternative energy source

MFCs are considered one of the trending technologies that can address the future energy crises and wastewater treatment. They enable energy recovery from wastewater producing low sludge compared to existing technologies [19]. The utilization of waste for bioelectricity or high-valued energy or chemicals is considered the best option to overcome the challenges associated with conventional wastewater treatment while adding value to waste products [20]. Kumar et al. [21] defined bio-electro-chemical systems (BESs) as the biosystems that convert the energy of organic wastewater substrate (chemical energy) into electric energy or high-valued products by employing indigenous *exo*-electrogenic bacteria [21,22]. As Gil et al. [23] reported, MFC performances may be influenced by many physical and chemical factors including supply of oxygen, cathode reduction, substrate oxidation rate, microbial electron transferring capacity to the electrode, the circuit resistance, and protons transportation toward the cathode through the membrane.

The important basic components of MFC are cathode and anode chambers (with anaerobic microbes), inter-connected cathodic and anodic electrodes, and the semi-permeable membrane that allows proton exchange (proton exchange membrane—PEM), an electrolyte medium [24]. MFCs depend on the electrochemically active microbial decomposition process that converts the chemical energy to electric

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energy. Certain bacteria are capable of releasing electrons to the surrounding medium during respiration. In MFCs, bacteria also require energy to survive, and they consume energy in two steps; (1) oxidation, (2) reduction. Oxidation reactions involve the release of electrons from organic matter, while in reduction, electrons are allowed to attach to the final electron acceptors (i.e., oxygen, nitrate). A semipermeable membrane or an agar salt bridge connects the cathode chamber and the anode chamber of the MFC that contributes a pathway to the movement of electrons released in oxidation. The movement of electrons generates a current [25].

## 2.1 The basic structure of the MFC

A typical MFC system can be either single-chambered or separated into individual chambers composed of the cathode and the anode compartments together or separately (Fig. 1). MFCs are occupied by microbial communities capable of producing electricity known as "eletricigens," or "exoeletricigens," or "anode respiring bacteria" that are capable of oxidizing complex organic compounds [22]. In the MFC anode chamber, organic energy stored as chemical energy gets converted into electric energy with microbial cellular respiration [25].

In the cathodic chamber, anaerobic microbes convert sugar into carbon dioxide, protons, and electrons under the anaerobic ambience ($C_6H1_2O_6 + 12H_2O$- - - - - - $6HCO_3^- + 30H^+ + 24e$) [26]. The generated electrons move into the cathode through the external load and interact with the protons and oxygen available at the cathode and get reduced to form water molecules ($O_2 + 4H^+ + 4e^-$- - - - - - -$H_2O$). This electron

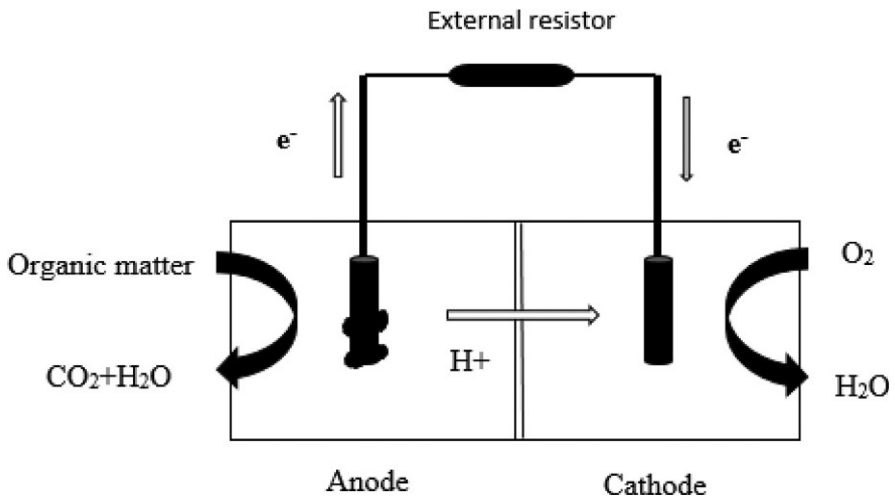


**FIG. 1**

Structure of a typical two-chamber microbial fuel cell (MFC).

*Source: S. Sevda, P.J. Sarma, K. Mohanty, T.R. Sreekrishnan, D. Pant, Microbial fuel cell technology for bioelectricity generation from wastewaters, in: Waste to Wealth, Springer, Singapore, 2018, pp. 237–258.*

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movement generates an electric potential between the cathode and anode and resulting in an electric power generation. Accordingly, the difference between the anode and cathode potential determines the MFC's electricity generation [27]. As oxygen molecules interfere with electricity generation, the anode compartment should be strictly anaerobic [28].

The power production of MFCs is intended as $P$ (W) = $I$ (A) * $E_{cell}$ (V), where $I$ is current, and $E_{cell}$ is the cell voltage at that point. $P$-value is usually related to the anodic surface power density (PD) and expressed as W/m$^2$. This formula is essential for the industrial implications of MFC on a large scale like water treatment plants, textile plants, or food processing plants [27]. Commonly, the maximum power generation of the fuel cell is calculated using a polarization curve, plotting cell voltage ($E_{cell}$) against the current ($I_{cell}$) at the variation of external resistance. The current intensity is conveyed concerning the surface area of the anode and is defined as current density (CD). Columbic efficiency (CE) is calculated based on the number of electrons that are transferred to the electrode with the number of electrons theoretically delivered by the substrate oxidation [27].

The electrochemical reactions are exergonic, which means the reaction possesses negative free reaction energy (Gibb's-free energy), which proceeds naturally with energy release (electric or electron release). The standard free energy is converted into a standard cell voltage [29]. A reaction's Gibbs-free energy measures the maximum capacity that can be obtained from a reaction of a thermodynamic system.

A positive standard cell voltage formed by the negative free reaction that discriminates a galvanic cell from an electrolysis cell, as the latter, associated with positive free reaction energy and thus with a negative cell voltage, requires the input of electric energy. The standard cell voltage is derived from the standard redox potentials of the respective redox pairs in MFC [29].

Theoretically, wastewater, sewage, and leachate have a high potential to be used in power generation for MFCs by breaking down organic matters into simple molecules by microbial involvement [30]. However, these technologies still under research; thus the limitations associated with MFC such as higher resistance (internal), high construction, and operation cost limit their scaling up for commercial energy production [26].

## 2.2 Components of MFC system

Conventional fuel cell devices directly transform chemical energy stored in organic matter into electrical energy. Bioelectricity is defined as the generation of electricity from living beings. Potter [31] presented the basic idea of MFCs, the first record of fuel cell studies. Early studies show two structures of MFCs, either single-chambered or dual-chambered [26]. MFC has four major components that affect electricity generation efficiency. Those are electrode material, mediators, membrane, anode medium, and cathode medium.

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### 2.2.1 Electrode materials

One of the significant challenges in the MFC is finding the proper electrode for efficient electricity generation. The materials used in MFC can affect the potential of MFCs [32]. The surface of an electrode is responsible for the flow of electrons; wide electrodes provide a greater amount of electrons, while thinner electrodes provide fewer electrons for the system. In earlier studies, scientists have used some carbon-based, graphite-based, and metal-based electrodes. For example, the electrode can be either carbon cloth, carbon paper, carbon felt [33], graphite-based like graphite fibre brush, graphite felt [26], graphite granules, carbon mesh [34] and platinum, platinum black, and activated carbon for anode and cathode material. Electrodes can be arranged differently to produce higher output like single, tubular, or multielectrode configurations [32]. An ideal electrode should be stable, biocompatible, and possess a higher surface area and electro-conductivity [26].

### 2.2.2 Mediators

There are two types of MFC. The first one is mediator-less, and the second one is with the mediator. No mediator MFC uses electrochemically active bacteria to transfer electrons directly to the electrode [35]. The second, the electron mediator, employs an external mediator to transfer electrons to the anode. An ideal electron mediator for converting metabolic reducing power into electricity should produce a reversible redox complex at the electrode. It should have a high negative E0 value to maximize electrical energy production. Good mediators should have the following features: (1) low cost of implementation; (2) facility in crossing the cell membrane quickly; (3) be nontoxic and nonbiodegradable to microbes; (4) have a high reaction rate of electrodes; (5) good solubility in anolyte; (6) able to collect electrons [36]. A few examples of the common mediators used in MFCs are thionine, methylene blue, neutral red, etc. [37]. Earlier reports have mentioned another critical way of electron transport, which is the use of self-produced mediator by anaerobic bacteria and a specialized structure called "nanowires" or "pilli of Geobacter sp." [38]. Though mediators enhance electron transfer capacity, most mediators are unstable and toxic to microbes. Therefore, the microbes capable of transferring electrons without the mediators are highly acceptable and known as mediator-less MFCs [35].

### 2.2.3 Membranes

MFC power generation is mainly affected by the proton exchange system between the anode and cathode compartments [39]. It can be either a cation exchange membrane [35] or a salt bridge [40], which is used to keep cathode and anode chambers separated and only allows protons to transport from anode to cathode chamber. The potential difference between the two chambers drives the electrons to run on the circuit, while microbial degradation of waste materials provides a substrate to generate bioelectricity [41]. There are many proton exchange membranes (PEM), and Nafion is considered the most popular membrane because of its highest selective permeability for protons. Nafion is expensive compared to other membranes. In addition to the higher price, ion exchange membranes, i.e. cation exchange membranes (CEM) and

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anion exchange membranes (AEM), cause some other problems to the MFC system, including pH splitting, biofouling, and high oxygen, and substrate diffusion [42].

### 2.2.4 Anode and cathode medium

The cathode acts as an electron acceptor in the electricity generation process in MFC. The cathode is generally exposed to air or other additional chemical electron acceptors like chromium, hexacynoferate permanganate, and azo dye [38]. Such chemicals are costly to use as electron acceptors at the cathode, and disposal can cause adverse environmental effects. Therefore, scientists are moving toward bio-cathodes with cyanobacteria or microalgae as a more sustainable solution [43]. They produce oxygen via photosynthesis, which ultimately acts as electron acceptors at the cathode while producing $H_2O$ as a by-product.

## 2.3 Advantages of MFC over other alternative energy sources

MFCs have operational and functional advantages over the current energy production from organic matters.

1. No intermediate products and chemical energy stored in organic substrates are directly converted to electricity (high conversion efficiency) [44].
2. MFCs operate well at ambient temperature and also in low temperatures.
3. There is no need for gas treatment in MFC because the off-gases are enriched in carbon dioxide and typically have no harmful environmental content [26]. No need for gas treatment in MFC because the off-gases are enriched in carbon dioxide and normally have no environmental harmful content [26].
4. As the cathode is aerated passively, there is no need for energy input for aeration.
5. MFCs have the potential for widespread application in locations without expensive infrastructures [19]. Also, there is a broad fuel availability for MFC. For example, wastewater, sludge and kitchen waste can be utilized. Less sludge production is also an advantage at the end. The bacteria growth yield is considerably low compared to anaerobic processes [26]. Furthermore, according to Zhang et al. [44], cost-effective bio-cathode and bio-anode development is the next paradigm of MFCs, namely microbes and cyanobacteria that could serve as the biological catalysts instead of expensive conventional materials (i.e., chemical and metals).

# 3. Water pollution and waste management

Waste management is one of the basic human requirements. It can often affect the provision of other associated facilities, including ground and surface water, odour fly issues, health care, energy, and other basic needs [25].

Water sanitation is one of the most basic human and environmental necessities due to anthropogenic activities. Water pollution is a globally emerging challenge. Leachates of solid waste are one of the significant causes of surface and groundwater

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pollution [45], and wastewater is known as one of the resources used for a myriad of purposes, such as energy and plant fertilizing nutrients [25].

Direct disposal of wastewater without proper treatment from both industrial and nonindustrial sectors (household) makes the water bodies susceptible to eutrophication that leads to surface water algal blooming, which has downstream effects such as developing hypoxia, or anoxia in water bodies that has adverse effects on the environment, social activities, as well as economy of the locality and country [45].

Landfill dump sites are becoming a significant problem, especially in urban areas. They are mainly recognized as one of the causes of pollution, i.e., solid waste disposal has been going on for years near groundwater sources. This has become a significant issue in both developed and developing countries. One of the environmental concerns related to landfill is the discharge of leachate with a high concentration of complex organic matters (e.g., chemical oxygen demand (COD) of 5000–20,000 mg/L) and ammonium-nitrogen (e.g., 3000–5000 mg/L), distinguishing it from municipal wastewater, which may cause serious problems such as contamination of ambient groundwater, eutrophication of water body, or odor release. Therefore, there is an urgent and timely need to treat landfill leachate to protect groundwater from pollution.

## 3.1 Different MFC systems for wastewater and leachate treatment

### *3.1.1 Wastewater treatment*

Wastes, especially wastewater, do not require capital and can be processed conventionally at the production location. Therefore, producing electricity from waste using MFCs is a sustainable and low-cost solution for addressing future environmental pollution and energy devastation issues. According to reports, domestic wastewater contains 9.3 times more energy than currently used in ttreating wastewater by conventional methods [26]. The MFCs can utilize this energy in the wastewater to a maximum; the produced bioelectricity can be stored and used for different applications. Wastewater treatment using cyanobacteria and microalgae is a well-established technology practised worldwide, but recent attention has shifted toward enhancing the value through algae cultivation . The low cell densities achieved in large-scale freshwater algae cultivation, low photosynthetic efficiencies, and the requirements of nutrients often become limitations in culturing algae for biodiesel production. Heterotrophic or mixotrophic cultivation of microalgae in wastewaters rich in minerals and organic content at least partially addresses this issue by achieving high cell densities and cheaper cost of production. Since this also serves to remediate the wastewater, it possesses a dual advantage. Algal biomass generated in wastewater physio-treatment facilities can serve as a source of oil for biodiesel. The residues generated are a rich source of cheap protein and biomass that may be converted by other means into fuels and chemicals [24].

MFCs represent a standard and emerging technology where microbial catalytic reactions at the anode result in electric power generation from waste and renewable algal biomass. MFCs also support the bioremediation of wastewaters like recovery of

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heavy metals, decolourization of dyes, and production of bioenergy such as biomethane and biohydrogen [46]. Thus, MFCs have the dual benefits that facilitate power generation and wastewater treatment, i.e., the means are eco-friendly and economically achievable [26].

MFCs act as bioreactors where chemical energy is transformed using anaerobic bacteria as a biocatalyst through the oxidization of possible biodegradable substrates. Therefore, the MFCs can be used for wastewater treatment while producing bioelectricity as a simultaneous process [40].

The MFCs are helpful in another way as a biosensor for determining chemical oxygen demand (COD) in industrial and natural wastewater produced by industries and water treatment plants. Combining the conventional system and MFCs may be a better solution to achieve promising results [24].

In the MFC anode, various substrates have been used for electricity generation with improved output in terms of power generation, and newer substrates from waste are brought under these systems. At first, simple substrates like acetate and glucose were commonly used as anode substrates, but in the contemporary, wastewater, sludge, and industrial sewage are used. Different kinds of substrates, from industrial waste to household waste present in wastewater in pure or complex forms, have been used in MFCs as the carbon source for bioelectricity generation and wastewater treatment purposes [43]. In many cases, MFC operating with naturally occurring microbial communities showed better results than MFC working with external bacteria additions to the substrates. Inoculum taken from previously operated MFCs give higher power outputs and overall performances in a short time [19].Acetate and glucose are the most common substrates, while sucrose [47] to is employed. It is challenging to compare MFCs performance because performance depends on different operating conditions such as surface area of electrodes, substrate concentrations, type of electrodes, and different microorganisms used. According to previous studies, microbial communities frequently studied in an MFC include *Saccharomyces cerevisiae* [31], *Escherichia coli*, *Proteus vulgaris* [48], *Geobacter sulfurreducens* [49], and *Shewanella putrefaciens* [50]. Performance of MFCs depends on multiple factors, including substrate concentration (organic load), nature of substrate, substrate degradation rate by bacteria, biofilm formation ability on the electrode's surface, external and internal resistance of the cell, mode of operation, and type of electrodes, etc. [51].

According to previous studies, Kim et al. [50] studied two-chambered MFC as a film bioreactor using anaerobic sewage sludge. Oh and Logan [52] reported glucose fermentation in food processing wastewater and simultaneous hydrogen and electricity production. Lovley [22] explained the electricigens like *Geobacter* and *Rhodoferax* as insights into the elegance of extracellular electron transfer. Lovely's work developed a better understanding of the application of electricigens. Reimers et al. [53] reported benthic MFCs coupled with biogeochemical reactions monitored for 125 days and recorded a maximal sustained power density of 34 $mW/m^2$ equivalent to 1100 $mW/m^2$ of the sea floor.

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### 3.1.2 Leachate treatment

Li and Zhao [54] stated that the conventional methods for treating leachate have several disadvantages. For example, physical methods such as sedimentation, adsorption, and membrane filtration or chemical processes such as coagulation and chemical precipitation require high costs, but the efficiency is considerably low. Aerobic biological processes are effective for removing organic carbon, but they also produce large amounts of excess sludge production, odor generation and high energy consumption. Anaerobic approaches, for example, upflow anaerobic sludge blanket (UASB) system has been reported to be able to remove COD from leachate with an efficiency up to 71%–92%. However, methane gas released during this process may contribute to global warming that makes it nonsuitable for zero carbon emission future [55]. Therefore, more economical pathways for efficient leachate treatment remain to be developed.

Leachate is considered a high concentration organic wastewater; therefore, a large number of organic substances can be utilized in MFC and turned into power. According to Youet al. [56], using landfill leachate as anode substrate, a maximum power density of 2060.19 $mW/m^3$ based on the anodic liquid volume was obtained at an external load of 1400 Ω in dual-chambered MFC. The same experiment was carried out with a single-chambered MFC, which provisioned the maximum power density of 6817.4 $mW/m^3$ at an external resistance of 150 Ω, almost 3.4 times higher than that obtained in the above-mentioned dual-chamber MFC. The above findings show the possible energy outcome from landfill leachate when used in MFC. Another contributory study shows the maximum voltage generated by the MFC as 434 mV with 0.33 Ω external resistance using cyanobacteria (*Microcystis* sp., *Spirulina* sp. and *Chroococcus* sp.) as cathode substrate along with leachate at the anode [43].

However, an MFC is still not a complete success in removing ammonium-nitrogen from leachate; there is still a prospect for MFC to be used in leachate treatment for more efficient reasons. For example. Complex organic matter in leachate can be directly converted into electricity without intermediate products and directly or stored in the power supply. Subsequently, COD removal is considered a partial treatment of leachate, occurring during power conversion and anoxic biodegradation of microbial community on organic matter in the MFC reactor system. If required, more efficient treatment of leachate by MFC can be followed by treating processes, used in contemporary practices such as activated sludge, biofilm units, or some chemical facilities at first (Shi et al., 2006).

## 4. Challenges associate with MFC

MFCs still have some drawbacks in terms of operation and maintenance. Drawbacks mainly include low power output and high operating cost, which is a massive barrier to the commercial success of the MFC technology. According to Rahimnejad et al. [57], the initial cost of the MFC implementation is 30 times higher than using a

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traditional activated sludge system for domestic wastewater treatment. The initial cost increases are due to expensive electrode materials, membranes, and cathode catalysts. Furthermore, the current and power density generated from wastewater using MFC is frequently less than expected, which is not competent and par with other renewables. High internal resistance, low mediator efficiency, low degradability of substrate and availability of microbial community are the main reasons for lower power output. Regarding high current and power output, stacked MFCs in parallel or series would be an effective solution for the above problems [58].

The stacked MFCs in parallel mode can increase the current and power density much higher than those assembled in series [57]. The stacked MFCs in direct series are capable of increasing the voltages, which are beyond the chemical fuel cell. Further research should be performed to improve the performance of stacked MFCs in direct series. Other than the above mentioned, MFCs experience internal losses that reduce the power output to an expected extent. Losses are mainly categorized as (1) activation losses, (2) ohmic losses, and (3) concentration losses [59].

## 4.1 Activation losses

An activation loss comes with the MFC structure and anodic bacterial community. There are two leading causes: (1) anode surface structure and surface area; (2) amount of energy gained by bacteria during metabolism. The single largest contributor is anode surface area [26]. According to Bower [59], in generalization, the higher the surface area, the anode has better fuel cell performance, and fewer activation losses are observed. The structure of the anode surface can also have an impact on activation losses. A surface with more biologically active sites will likewise improve the performance of an MFC. Both are due to the higher stability of the biofilm attached to the anode electrode and, consequently, the more electrons the electrode can collect [59].

The bacterial metabolic losses that occur are based on two main components. First, the closer the MFC's operating conditions match the bacteria's optimum environment, the better the bacteria's metabolism and, therefore fuel cell performance [59]. The second, and more complex component to alter, is the electrochemical advantage of the bacteria using the electrode as the electron acceptor instead of other chemical species in the anolyte [59]. The higher the electrochemical potential of the reaction for the given electron acceptor, the more likely the bacteria are to choose it. This means that the anode's potential plays a significant role. The closer to zero volts the anode can be maintained, the more energy the bacteria can gain from using the anode as the electron acceptor. Therefore, the more energy the MFC will be able to produce [26].

## 4.2 Ohmic losses

Ohmic losses represent a significant portion, though not all based on internal resistance of an MFC and thus as the name would suggest, are actually measured in ohms. Ohmic losses within MFCs can be caused by any of a great variety of conditions

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within the fuel cell [26]. They can be internal resistance of electrodes used, the connection of bacteria-electrode at the interface, conductivity of the anolyte and membrane, rate of ion transport across the membrane from anode to cathode, conductivity of the cathode substrate, etc. [59]. Even though ohmic losses have the largest number of causes, most of these can be avoided with careful planning and implementation. This is because most of these causes are subject to factors of the fuel cell design and operating conditions.

### 4.3 Concentration losses

Concentration losses are most commonly taken as mass transfer losses while operating. As bacteria consume nutrients, the concentration of organic compounds near the bacteria begins to reduce with time. Therefore, it causes a nutrient reduction from initial concentrations, and this phenomenon drives the system toward a complete lack of substrate at degradation sites. Electricity generation is proportional to the concentration of degradable organic matter concentration. As a solution, batch systems of organic matter that are neither stirred nor agitated can be fed into the system. Stirring, agitation, or running the fuel cell in a continuous flow mode can all reduce or negate these losses partially or entirely [59].

## 5. Advantages of cyanobacteria-based MFC over other MFC systems

The hydrogenase enzyme oxidises ferrodoxins in the presence of anaerobic conditions in cyanobacteria, and hydrogen is produced as a byproduct of that reaction. Furthermore, cyanobacteria can be used in bio electrochemical systems in different ways. First, they can be used at the anode as an electron donor or to remove organic matter from wastewater. Then at the cathode, the electron acceptor is produced through photosynthesis. For example, the photosynthetic microalgae (*Chlorella vulgaris*) have been studied in cathodic half cells in MFCs [60]. *Microcystis* sp. and *Chroococcus* sp. have been tested as cathode mediums to evaluate the competent power generation, and the results suggest *Microcystis* sp. is more prominent for usage in MFC [43].

Due to some operational complications, the MFC performance is still limited to a smaller scale. To improve to a more extensive scale, use can be done through the oxygen reduction reaction (ORR) for the cathodic half-cell as an alternative to expensive chemical catalysts. The idea of bio-cathodes is a feasible alternative to chemical and metal cathode catalysts, improving the cost-effectiveness of MFC in an environmentally friendly manner [61]. The use of green algae as biocatalysts in the cathode half-cell is to fulfil the oxygen requirements for the ORR as an electron acceptor and produce biomass to use as fuel for the MFC anode [62].

Using photosynthetic cyanobacteria is considered one of the most promising solutions as it can fix carbon throughout the process, which is a significant advantage while undergoing electricity generation and wastewater treatment [63]. Implications

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on a large scale would also benefit from low-cost biomass regeneration ability in a smaller space and nutrient recovery at the end of the cycle for use as putative fertilizers.

Using cyanobacteria as the electron acceptor in the cathode, as an alternative to chemical compounds, is environmentally friendly and readily available in water bodies worldwide [43]. Higher yields can be obtained in a small space under laboratory conditions. Cyanobacteria in water bodies are considered nuisance organisms that contribute to many environmental and health issues. Using cyanobacteria in the cathode helps benefit from their presence as they participate in the MFC's wastewater treatment process by completing the electron flow. According to the study by Gajda et al. [62], it is shown that the maximum power generation using algal-based cathode produced 128 mW. In comparision, while abiotic MFC produced only 46 mW at the same time. This means the effectiveness/efficiency of the cathode with cyanobacteria is a more promising alternative in energy generation than the chemically induced cathode.

According to Logan et al. [26], greater power densities can be obtained using mixed cultures in MFC than those with pure culture. Most of the eutrophic water bodies bear some cyanobacteria species as algal blooms. They can be easily collected and cultured and used as the biocathode in the MFC system in a cost-effective and environmentally sustainable manner.

When microalgae are used as anode compartment, they depend on the end products of bacterial metabolism (for example, $CO_2$ and ammonia), and subsequently, they supply oxygen for aerobic bacteria for the degradation process. This process can increase resource efficiency turning eutrophication into an opportunity for electricity generation and biomass production.

According to Commault et al. [64], the standard overall reaction for photosynthesis occurred at the cathode as follows. $CO_2 + 12H^+ + 12e^- \text{- - - - - - - - - } C_6H_{12}O_6$ (biomass) $+ 3O_2$. In the reaction, $H^+$ and $e^-$ are normally supplied by water molecules. If there is an alternative electron donor in the compartment, cyanobacteria may use it in photosynthesis [64].

Powell et al. [65] investigated a photosynthetic biocathode based on the microalgae *Chlorella vulgaris* to fix carbon. The study suggests that some mediators were found to affect the growth rate. When used in a MFC configuration, the growth rate of *C. vulgaris* was much lower in the presence of methylene blue. The main reason for this is the difficulty of light penetration to cyanobacterial cells due to the mediator in the solution [65].

Many factors affect the growth and performance of cyanobacteria in MFC. $CO_2$ concentration has a significant effect on growth rate [64]. Optimal growth rates were obtained when $CO_2$ was mixed with air between 5% and 10% and added to the medium. On the other hand, it was found that under light conditions, they increased the growth rate in a MFC by a factor of 1.7 [65]. The pH of the medium was found to have low effects on the growth, as some *Chlorella* species can utilize $CO_2$ in both dissolved forms. Many microalgae provide an advantage to using the native $CO_2$ form, which negates the lower pH media.

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## 6. Future perspectives of MFC

At first, MFCs were used as an electricity generation method while benefitting from wastewater treatment [55]. Different substrates, electrodes, membranes, and chemicals were used from initial MFC to novel MFC to overcome implication and operational problems. As a result, MFCs have metamorphosed into a more advantageous system for electricity generation and wastewater treatment in large-scale applications. Scientists are still working on introducing more efficient, cost-effective, and successful MFCs with minor drawbacks. Recently, a chemical modification of anodic surface using nitrogen-containing amines has shown higher and more rapid electrical current production when placed in microbial cultures [66].

While upgrading the MFC systems, scientists have realized that it is not very easy to compete with existing energy sources from an economic and environmental point of view. Therefore, a development pathway to initiate new applications of MFCs from electricity production to different areas of other specialized applications addressing the environmental problems is now an emergent horizon. Such mechanisms have invented many important applications for the world.

The MFC-based biosensor is another application that can be applied in different environments to monitor microbial activity, organic matter, and toxicity in eutrophic waters [67]. BOD monitoring is one of the applications of MFC-type biosensors since the current generation depends on the anode microbial respiration proportional to the fuel concentrations [35]. Several types of MFC-based biosensors have been developed for monitoring BOD in different water sources such as surface water, industrial effluent, or treated wastewater samples. Results showed upright steadiness, accuracy, and wide detection range of compounds that can be successfully implemented in industrial levels [35]. The relationship between the Columbic efficiency of MFCs and the concentration of organic substrate in the wastewater was firstly employed for BOD monitoring. Another technique that can be used in many settings to track microbial activity, organic matter, and toxicity in eutrophic waters is the MFC-based biosensor [67].

A recently proposed MFC application is toxicity monitoring based on the electrical current inhibition principle, which can be used as a good indicator for the appearance of toxicants [48]. Chemical toxicants can inhibit the metabolic activity of electrochemically active microorganisms, which can later inhibit the transfer rate and ability of electrons to be transported to the electrode,ultimately resulting in a decrease in the electricity production of MFC. Therefore, it is proposed to use MFCs as a toxicity sensor for checking the existence of chemical toxicants in various environments polluted with point and nonpoint sources [67]. Patil et al. [68] investigated the effect of biocides on wastewater-derived microbial biofilms. They showed that the antimicrobial agents greatly affected the current generation of mediator-based MFCs enriched with planktonic cells derived from wastewater sources.

Mehanna et al. [69] reported an invention of a new method, a modification of MFC to reduce the salinity of saltwater while generating power, which is called To microbial desalination cell (MDC). This technology is useful for countries

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surrounded by oceans with drinking water deficiencies. Another modified application of MFCs is microbial electrolysis cell (MEC), which has revealed auspicious usage for energy-rich chemicals like hydrogen and $H_2O_2$ derived from carbohydrate-rich wastes [70,76,78]. The knowledge gained from successful applications will improve the energy production of MFC-based technologies. One main limitation of the MDC reported is the voltage variation over time in the desalination process. An alternative approach is to increase the voltage using a power source and produce hydrogen at the cathode [69]. It can be seen as collaboration of MEC and MDC technologies together, which offers to desalinate saltwater, produce hydrogen, and possibly treat wastewater simultaneously at the same time.

Lately, the application of photoautotrophic cyanobacteria to produce a small-scale MFC, named a bio photovoltaic (BPV) cell that operates without an added carbon substrate, has been developed. Thus, BPV devices can produce power in both the light and the dark, in contrast to photovoltaic (PV) systems driven solely by light and are more durable [71,77]. These features suggest that BPV devices could use in low-power applications as an environmentally friendly solution.

According to Oh et al. [72], innovation in designing new MFC reactors has been influenced by the need for higher power output under low operational costs. Therefore, materials that reduce internal resistance, designs that provide the highest surface area for anaerobic bacterial attachments, and alternatives to expensive metal catalysts at the cathode have attracted the scientific community's attention [72]. Köroğlu et al. [73] have developed an up-flow multitude MFC (UM2FC) to treat the retained part of the membrane process and such electricity production using an air-cathode UM2FC inoculated with sediment and recorded efficient treatment over conventional MFC. Mathuriya [74] studied a multiple anode chamber MFC design (MAC-MFC) using more than one anode chamber in a single unit to access the power output. Results demonstrated that MAC-MFC produced steady and higher power outputs than single-chambered MFC, and each anode chamber contributed efficiently to the system. Simultaneously, MAC-MFC efficiently cost-effectively treated different kinds of wastewaters and utilizes a small space that makes it a promising application in future. Timmers et al. [75] have investigated the tubular plant MFC to improve the MFC application. According to the study, the roots of a plant provide the electrochemically active bacteria through the degradation of dead roots. They act as substrate-degrading bacteria at the anode and provide electrons to the system through the electrode inserted at the anode. This process does not need to harvest the plant while generating electricity. This means this technology avoids the consequences of food production and can be implemented on agricultural lands. Furthermore, the PMFC technology can be introduced to locations identified as unsuitable for food cultivation.

## 7. Conclusion

With the emerging energy crisis, there is a crucial need for an alternative energy source to fulfil the demands of the globe in an environmentally sustainable manner. Subsequently, with increasing population and industrial development, wastewater

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accumulation has become a burning issue. MFC is one of the most recent technological solutions to address these issues simultaneously. Different MFC systems have been developed to find the most successful setup and address environmental problems beyond wastewater purification, such as bioremediation, bio-sensors, and desalination. The most recent advance is to use bio-cathode in MFCs as an environmentally friendly method. This technology uses cyanobacteria as an electron recipient at the cathode and produces $H_2O$ as a byproduct. Cyanobacteria possess many advantages over conventional cathodes with chemicals; for example, low cost, easy disposal, easy maintenance, fast regrowth and a host of other conveniences. Therefore, it is expected that this cyanobacteria-based MFC will succeed in the future in the duality of electricity generation and wastewater treatment as an environmentally friendly, low-cost energy solution.

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CHAPTER

# Bioelectrochemical systems: Basic concepts and types

8

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## 1. Introduction

A new revolutionary feature of bioengineering technologies is the use of bioelectrochemical systems (BES) that implement bio-based catalysts or microorganisms with electrochemical methods that help in improving reduction or oxidation of metabolism. Generation of electrical power or reduction reaction can be achieved by the use of BES involving the transfer of electrons between electron acceptor and electron donor [1]. The concept of BES is widely applied for the development of microbial fuel cells (MFC). MFC implements microbial species that convert chemical to electrical energy with the utilization of various types of substrates especially wastewater and organic compounds [2]. It is further observed that microbial electrolytic cells show antagonistic effect as compared to MFCs as they convert electrical energy to chemical energy mediated by the microbial systems using enzymes that help in the production of useful compounds like methanol, ethanol, or hydrocarbons and formate. These chemical compounds are converted to alternate fossil fuels [3]. BES has shown its efficacy as alternate, green, and sustainable system for the generation of energy [4]. Two common examples of BES are microbial electrolysis cells (MECs) and MFCs that also have immense role in maintaining environmental sustainability. The regular mechanisms of treating wastewater do not possess the ability of utilizing various complex organic and inorganic chemical compounds that are toxic in nature. Similarly, the electrochemical process also possesses some limitations in the treatment of wastewater in terms of its additional generation of wastes and energy input.

*These authors contributed equally to this work.



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Thus, BES possesses the ability to combine both electrochemical and biological processes bringing about maximum remediation of wastes being present in the effluents and also results in the generation of electricity, useful chemicals, and hydrogen. BES thus involves the concepts of multifaceted subjects comprising of microbiology, biotechnology, environmental science, and electrochemistry. The energy being liberated by the operation of BES results in the process of microbial electroremediation and thus helps in the treatment of wastewaters and other types of pollutants that are associated with it. This chapter would focus on the basic concepts and types of various BESs that can be utilized for the performance of treating wastewater.

## 2. Mechanism of working of BES

Generation of energy by the microbial metabolism comprises of both anabolism and catabolism that is a combination of respiration and fermentation processes. This process requires an electron source that is associated with the flux of the microbes and effective electron sink for the completion of electron transport chain. The processes of respiration and fermentation remain separated by permeable membrane within a system possessing electrodes that result in the development of environment for harnessing energy being liberated by the activities of the microbial cells [5]. The microbes possess the ability to produce reducing equivalents and electrons at the anode. The transportation of protons takes place to the cathode via the electrode solution, the selective membrane thereby generating a potential difference between the cathode and the anode facilitating the flow of electrons through the circuit across the available external load [6]. There are multiple applications of the reducing equivalent being produced by BES in the process of remediation that can be categorized as power generation, wastewater treatment, and the recovery of value-added products. The generation of power can be achieved by the process of substrate metabolism that undergoes the process of oxidation in the presence of the electron acceptor. The wastewater also serves as a donor or acceptor of electrons thus results in the enunciation in the mechanism of remediating wastewater via anodic oxidation and cathodic reduction [7]. It has been further observed that the mechanism of reducing carbon dioxide ($CO_2$) or other substrates is being adapted for its commercial viability [8].

### 2.1 Anodic mechanism

The reactions taking place at anode play important role in the treatment of wastewater by the involvement of microbial metabolism, which helps in the induction of electrochemical oxidation (EO) mechanisms. Direct and indirect anodic oxidation mechanisms also follow two possible ways for the purpose of performing treatment of pollutant within BES. Degradation of substrate within anode is controlled by the presence of oxygen in the cathode chamber that also acts as terminal acceptor of

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oxygen. The ability of the cathode to accept electrons results in the enhancement in the flow of electrons within the circuit that are being liberated by the metabolism performed by bacterial species. Various types of oxidizing agents like bromine, ozone, and chlorine enhance the difference in the potential between the two electrodes thus developing the redox potential [9].

$$O + e^- \rightarrow O^*$$

$$O^* + E\,[] \rightarrow E\,[O^*]$$

$$S + E\,[O^*] \rightarrow S - O^* + E\,[]$$

'O' represents oxidant and O* represents excited oxidant

$$H_2O + E\,[] + Cl^- \rightarrow E\,[ClOH] + H^+ + 2e$$

$$C + E\,[ClOH^-] \rightarrow E\,[] + CO + H^+ + Cl^- + e^-$$

$$H_2O + E\,[ClOH^-] + Cl_2 \rightarrow E\,[] + ClO_2 + 3H^+ + 2Cl^- + e^-$$

$$O_2 + E\,[OH^-] \rightarrow E\,[] + H_2O_2H^+ + e^-$$

## 2.2 Cathodic mechanism

Like anode, cathode also plays an effective role in remediating waste streams and various types of pollutants like nitrobenzene, azo dyes, nitrates, and sulfates. The pollutants that are associated with the wastewater act as terminal acceptor of electron that helps in completing the circuit in the absence of oxygen. Thermodynamic hierarchy plays an important role in maintaining the functioning of electron acceptor. The cathode can be maintained at various types of microenvironmental conditions to enhance the treatment of various types of pollutants [10]. In case of normal cathodes, oxygen acts as a terminal acceptor of electrons, but biocathodes use microorganisms as catalyst to bring about terminal reduction reaction. The biocathodes possess a wide range of applicability to perform cathodic reactions. In cathodic reactions occurring at aerobic conditions results in the higher removal of substrate. The maintenance of cell potential for a longer period of time can be achieved by the mechanism of gradual substrate oxidation taking place at anode thereby enhancing its efficacy in treating wastewater [8]. The various treatment mechanisms that are associated with the system result in the initiation of bioelectrochemical reactions for the purpose of enhancing the removal of pollutant are as follows:

$$H_2O + c - a \rightarrow c^- + a^+ + H^+ + OH^- \tag{8.1}$$

$$H_2O + CO_2 \rightarrow H^+ + HCO_3^- \tag{8.2}$$

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$$HCO_3^- + c^+ + H^+ + OH^- + e^- + O_2 \rightarrow cHCO_3 + H_2O \quad (8.3)$$

(c is considered to be the cationic and a is considered to be anionic species)

$$c - a + E\,[] + H_2O \rightarrow E\,[c^+] + a^- + H^+ + OH^- \quad (8.4)$$

$$E\,[c^+] + H^+ + OH^- + e^- + O_2 \rightarrow E\,[] + c - OH + H_2O \quad (8.5)$$

## 3. Types of BES

### 3.1 Microbial electrochemical system

The direction of the transfer of the electron and the associated chemical reaction categorized microbial electrochemical systems into MFCs or microbial electrosynthesis cells (MECs). Microbial species act as catalysts on the anode chamber within the MFCs and possess the efficiency of generating electricity by the use of various types of the substrates. In MFCs, the electrons that are liberated by virtue of microbial metabolism are transferred to anode followed by capturing by cathode by virtue of external circuit that is used for reducing oxygen, and another liberated electron is responsible for the production of current [11] At recent times, MFCs showed its efficacy in treating wastewater by the utilization of pollutants for the generation of energy [12]. Diverse microbial species like *Shewanella putrefaciens*, *Escherichia coli* DH5α, and *Shewanella oneidensis* are utilized successfully within the MFCs for the generation of maximum power [13]. Bacterial cells within the MFCs act as catalyst for the transfer of electrons. The stability of the reactions associated with the microbial species is dependent on the external environment and various environmental factors this shows one of the drawback associated with MFCs [14]. Another drawback associated with MFCs are its development of internal resistance by the mechanism of proton exchange that results in the development of low power and current density [15].

MECs use microbial cells as catalysts, and the cells associated with the chamber of cathode act as acceptor of electron thereby enhancing intracellular metabolism [16]. The activities performed by MECs are opposite to MFCs. It has been observed that oxidation reactions occur within the anode chamber, whereas the electrons that are released are being transferred to that of the cathode. The potential associated with cathode is a significant characteristic of MFCs that is determined by the addition of electron shuttles and bacteria. The development of potential at the cathode is not same as that of theoretical difference in potentials as loss of energy take place by the electrons within the electrochemical system [17]. The scaling up of electrons within the MECs has various limitations which involve low energy efficiency and low rate of production [18]. Chemical incompatibility between biotic and abiotic catalysis is another common limitation of MECs [19].

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| Strains | Electron shuttles | Cathode electrode | Anode electrode | Substrate | Power output | References |
|---|---|---|---|---|---|---|
| *Shewanella oneidensis* | Flavins | Carbon cloth | Carbon cloth | Lactate | 2630 mW/m$^2$ | [20] |
| Consortium | NA | Carbon fiber | Ammonia-treated carbon cloth | Cellulose | 5.4 mW/m$^2$ | [21] |
| Anaerobic sludge | NA | Carbon cloth | Activated carbon cloth | Wastewater | 142 mW/m$^2$ | [22] |
| Recombinant consortium | Flavins | Carbon cloth | Carbon cloth | Glucose Xylose | 104.7 mW/m$^2$ | [23] |
| *Geobacter sulfurreducens, Escherichia coli* | NA | PTEE carbon cloth | PTEE carbon cloth | Acetate | 9.8 mW/m$^2$ | [24] |
| Activated sludge | NA | Modified carbon cloth | Modified carbon cloth | Sodium acetate | 2355 mW/m$^2$ | [25] |
| Anaerobic sludge | NA | Graphite felt | Graphite felt | Glucose | 28.6 mW/m$^2$ | [26] |
| *Geobacter* biofilm | NA | Modified graphite rod | Modified graphite rod | Acetate | 100 mW/m$^2$ | [27] |
| *Shewanella oneidensis* | – | CP/G/Au | CP/G/Au | Lactate | 508 mW/m$^2$ | [28] |
| Activated sludge | NA | Bilirubin oxidase | Carbon brush | Acetate | 6530 mW/m$^2$ | [29] |
| *Spartina anglica* | NA | Plant root | Plant root | Wastewater | 679 mW/m$^2$ | [30] |

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### 3.2 Enzyme-mediated electrochemical system

Enzymes can also be used as catalyst for bioelectrochemical system. The electrodes possessing enzymes act as external donor of electron and also acceptor [31]. Enzymatic reaction is a type of sole reaction taking place within electrochemical system that helps in predetermining the transfer of electron kinetics, and oxidoreductase is produced from the surface of the electrodes. Studies have shown the NADH-quinone complex I when fixed on the surface of gold-modified electrode results in the transfer of electron and proton to the electrode that acts as an acceptor of electrons [32]. Enhancement of high-density output of current was achieved by enhancing the load of enzyme thereby increasing the rate of catalysis [33].

## 4. Transfer of electron in bioelectrochemical system

### 4.1 Extracellular transfer of electrons

Oxidoreductases are the type of enzyme that is purified and fixed on the surface of electrochemical systems that act as modified surface for the purpose of accepting and donating electrons along with its interaction with the electrodes [34]. It has been further observed that transition between electron transfer and electron carriers has restrictions of the distance between electron carriers within the enzyme increases that will further bring about reduction in the transfer of electrons and enzymatic reactions [35]. Modification of electrodes is achieved to facilitate enzyme immobilization thereby effectively enhancing the effective transfer of electrons between the electrodes and oxidases [32]. Long distance transfer of electrons can be achieved by the use of long distance transfer of electrons [36].

### 4.2 Extracellular transfer of electrons

Apart from enzymes, microbial species play an important role as catalysts within MFC and MECs. It has been observed that the reducing equivalents that are stored as organic compounds are released as electrons that are further taken up by anode and transferred to cathode via external circuits resulting in the generation of electricity [29]. Voltage is poised at the cathode within MECs. Electrons that are released by the cathode during the time of energy metabolism and intracellular reduction are taken up by strains [37]. Various substances exhibit various types of electrochemical behaviors by incorporating various mechanisms of transfer of electrons between electrodes and microorganisms. Nanowires are conductive pili present on the outer membrane that acts as exogenous and endogenous shuttles of electrons [38]. The nanowires are present on the outer membrane of cytochromes that play an important role in capturing electrons within electrochemically active strains. Formation of biofilm enhances the mechanism of extracellular transfer of electrons having a beneficial role in the entire process [39]. Biofilm helps in the long distance transfer of electrons, higher rates of catalysis, and enhancement in the power output. Recent

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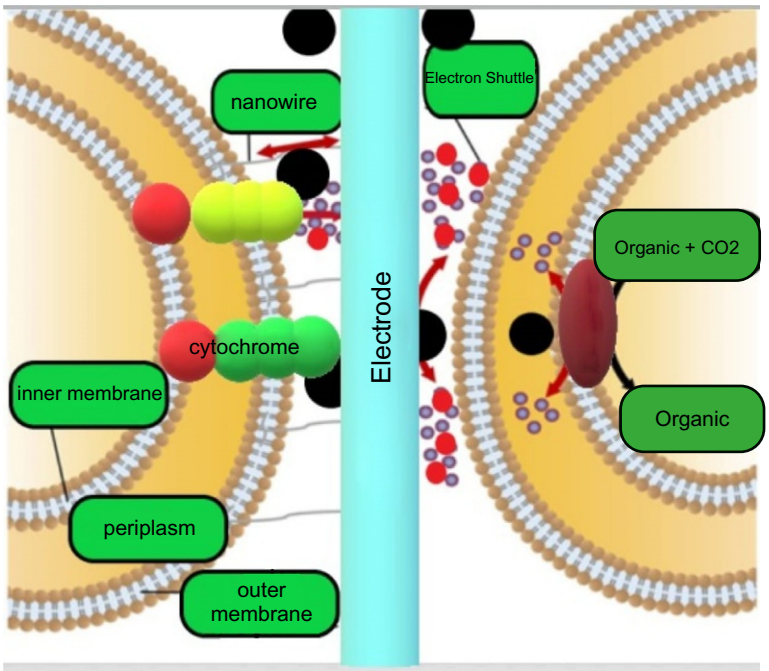


**FIG. 8.1**

Mechanism of bidirectional electron transfer between bacteria and electrodes.

studies have shown that modified porous materials are used in facilitating the development of biofilm on the surface of electrode [25]. The presence of three-dimensional surfaces in MFCs enhances the power output, but it is also dependent on the material constituting the electrodes [40] (Fig. 8.1).

## 4.3 Interspecies transfer of electrons

The activation of electrochemical system after incubation of microbial species requires some time. Strains that are electrochemically active help in transferring electrons directly to the surface of the electrode comprising of biofilm resulting in the generation of electricity [28]. Consortia of bacterial cells comprising of *Methanosarcina* and *Geobacter* help in the electro-synthesis of methane by virtue of transfer of electrons between species [41]. The transfer of electrons between the species helps in the enhancement of the symbiotic relationship thereby enhancing the production of biofuels by the use of cheap raw materials [41]. It has been observed that conductive material helps in transferring of electrons between species thus enhancing the coculture fermentation. Introduction of one or more microbial species helps in the enhancement of transfer of electrons and shuttles of electrons that can be used for indirect enhancement of transfer of electrons within the strains. The transfer of

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electron is associated with active carbon particles that occur within the cells and does not depend on cellular conductive structures [42].

### 4.4 Intracellular transfer of electrons

Strengthening of the interactions between electrodes and cells can be achieved by electron shuttles, nanowires, and modification of the electrodes. The intracellular transportation of electrons comprises of various electron donors and acceptors along with the synthesis of ATP [43]. The cytochromes that are attached with the membrane result in the transfer of electrons and performing intracellular metabolism for the electrochemically active bacteria [44]. Various types of electrochemically active bacterial species like *Geobacter* and *Shewanella* possess the ability to perform intracellular transportation of electrons and thus possess wide applicability within MFCs [45]. The bidirectional transportation of electrons can be achieved by the existence of potential differences available between the electron donors and electron acceptors [46]. It has been further observed that ubiquinone is adopted by MFCs and menaquinone are adopted by MECs comprising of lower levels of potential differences.

## 5. Applications in wastewater treatment

The efficiency of treatment by BES is dependent on the composition of substrates that are present within the wastewater. BES possesses the ability of utilizing various types of substrates as electron acceptors or electron donors comprising of both organic and inorganic molecules. The efficiency of the recovery of electrons depends on the oxidation state of the electron donors and the amount of microbial species present for allowing the mechanism of oxidation. The commonly used substrate for BES comprise of acetate and glucose along with some other carbohydrates like dextran, peptone, starch, sucrose, and ethanol that possess the ability to generate power. BES possesses the ability of utilizing complex organic wastes as substrates for the generation of power. The wastes that are biodegradable in nature and have its source from household activities, dairy industry, and vegetable waste have the ability of generating large amount of power. Thus, MFC possesses the ability of converting wastes to bioenergy.

### 5.1 High and low biodegradable component of wastewater

Wastewater is characterized by the amount of raw materials being present within it. Domestic wastewater comprise of various wastes that are biodegradable in nature and can be used as a substrate for BES [47]. The wastewater coming out from dairy industry comprise of milk-based components like proteins and lactate, which possess high efficiency of power generation [48]. Wastewater comprise of various sources of organic carbon in the form of proteins and carbohydrates, which can be easily

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degraded by bacteria. The energy that is being produced is very high with respect to the efficiency of the treatment. The performance of the microbes is found to get enhanced in the presence of high organic compounds. It has been also observed that BES possesses the ability of handling highly complex low degradable wastes that are associated with the wastewater. The complex nature of the waste creates problem in the conversion of complex wastes to some reducing equivalents and the subsequent generation of electrons and protons would be accepted by the wastes themselves causing further oxidation and development of low current densities.

### 5.2 Integrated processes for the treatment of wastewater

BES plays an important role in degrading the effluents by the process of preliminary treatment and fermentation processes comprising of solvent and acid metabolites with lesser amount of residual organic carbon. Studies have also demonstrated that variation in the organic content being present within the effluents the generation of power varies within the MFCs. Presence of various acids and metabolites like butyrate and acetate helps in the enhancement of efficiencies and enhancement in the power output [49].

## 6. Conclusion and future prospects

Microbial electrochemical cells work on the principle of mutual interchange of chemical to electrical energies. Energy conversion is an important factor for most of the BES and depends on the efficient transfer of electrons involving microbial electrochemical technology. The intra and extracellular electrons act as an important agent to bring about reduction in metabolism within BES. Conductive pili of nanodimensions act as a rich source of exogenous and endogenous electron shuttle that play an important role in capturing electrons within electrochemically active strains. Syntrophic association of microbial cells of same or different species leading to biofilm formation eventually leads to efficient long distance transfer of extracellular electrons, higher rates of catalysis, and enhancement in the power output thereby producing better results.

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CHAPTER

# 9 Anode modification: An approach to improve power generation in microbial fuel cells (MFCs)

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## 1. Introduction

Depleting fossil fuels/natural gas and looming energy crisis in recent decades have forced the researches, stakeholders, and government agencies to find alternative source of energy emphasizing on zero emission and reduced carbon footprints. Meanwhile, existing renewable energy sources have been promoted and modified to bring desirable improvements. Electrochemical systems such as fuel cells are an alternative energy source, devised to produce electric current/hydrogen gas. Fuel cell is a kind of galvanic cell/voltaic cell, which produces energy driven by expensive metal catalysts (platinum, palladium, etc.). Although fuel cells show good efficiency and come with zero emission with less polluting gases and negligible noise pollution, they suffer from main disadvantage of high cost accompanied by expensive catalysts and increased mass generation [1]. In an effort to eliminate high cost, microbial fuel cell (MFC) was devised where microorganisms drive the reaction to produce bio-electricity [2]. Apart from bioenergy generation and wastewater treatment, other novel features derived from different MFC prototypes include synthesis of bio-commodities, water desalination, waste heat recovery, and environmental monitoring using MFC-based biosensors [3–6]. MFC because of its promising benefits is studied extensively to get over every possible bottle necks and improve the overall efficiency. Oxygen is an important component of catholyte as it acts as terminal electron acceptor and gets reduced to produce electric current. Contrary, when oxygen enters anolyte, the redox reaction gets inhibited [7]. Therefore, construction of an idealistic MFC reactor is very crucial which ensures absolute separation of bacteria from oxygen. Moreover, the efficiency of the MFC is largely dependent on factors such as, nature of substrate, microbes, material used for proton exchange, ionic strength of the substrate, type of electrodes, and electrode spacing [8]. Among these, high-performance electrodes (anode and cathode) are central component because the



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power output is directly dependent on the material of the electrodes. Therefore, electrode material and its modification is focused significantly for achieving enhanced efficiency. Studies evidence that nature and structure of anode material limits the high-power output in MFC. The structure of anode determines bacterial adherence, which in turn affects the oxidation of substrate, electron transfer rate, and redox mechanism. Moreover, the anode acts as a sink for the electrons produced from bacterial metabolism. The desirable features for anode material include high conductivity, stability in the presence of microbial consortia, strong biocompatibility, noncorrosive nature, low resistance, high mechanical strength, high specific surface area, and durability. All the requisite features may not be available in a single material, therefore anode modification can be primarily used to achieve the required characteristics to improve the anode performance. Anode material is modified using several compounds such as conductive polymers (polypyrrole and polyaniline), metal oxides, nanomaterials, and many others. The present chapter discusses the importance of anode material in bioelectrochemical systems, highlighting on the innate properties of base electrode and development of new properties by modifying the electrode through deposition/doping particles or chemical alteration. This chapter also exclusively depicts about MFC, anode materials widely utilized in MFC, and different advancements made to improve the anode performance and enhanced energy generation.

## 2. Microbial fuel cell

As wastewater is considered to be an important energy resource, the energy contained in it can be drawn off using different processes. MFC can be one such process that harvest energy from organic fraction of wastewater. MFC is an advanced bioelectrochemical device, which renders sustainable wastewater treatment process with zero energy input. The chemical energy of organic substrate is converted into the electrical energy with the help of microbes. The MFC is configured into two chambers: anaerobic (anodic) chamber and aerobic (cathodic) chamber separated by ion exchange membrane. Unlike other electrochemical devices, in MFC, the redox reaction is catalyzed by active anaerobic biofilm forming microbes developed over the anode. The microbes oxidize the carbon source present in the substrate for its growth requirement and results in the production of electron, protons, and other metabolites. The electrons are directed toward the anode via intracellular/extracellular electron transfer (EET) mechanism and further channelized toward the cathode via external circuit. The protons travel across the ion exchange membrane to reach the cathode and react with electrons near the cathode to produce electric current. The redox mediators/electron shuttles were used to achieve better efficiency during the MFC start-up phase [9,10]. Scientific studies, post 1999 reported that MFC can run without redox mediators [11,12]. Henceforth, based on the mode of transfer of electron from substrate to anode, MFC can be categorized as mediator driven or mediatorless MFC.

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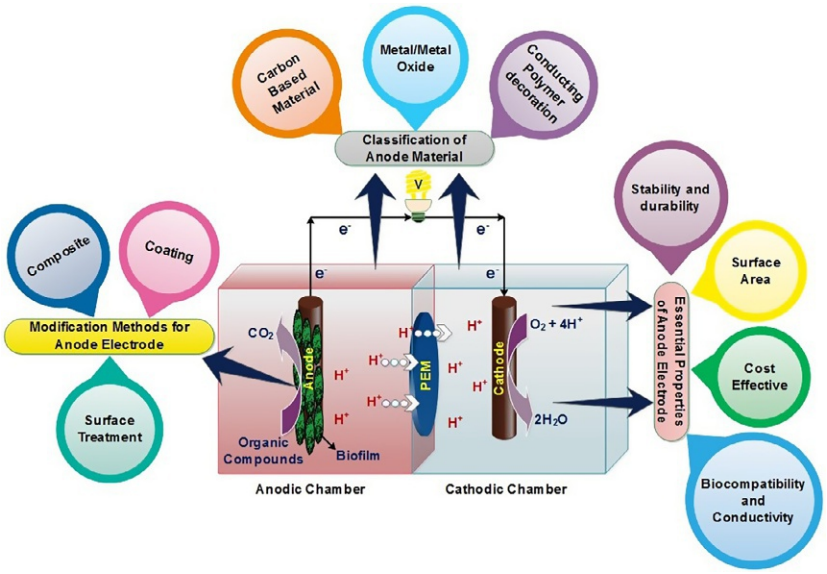


**FIG. 9.1**

Microbial fuel cell and anode modification.

Over a period of time, a large number of studies were performed to bring in significant improvements in the MFC. Nevertheless, some challenges are still encountered during scaling up and practical applications. Instability in anodic and cathodic chamber, high membrane resistance during transfer of protons, and limited power output are some of the major constraints worth mentioning [13]. The output of power depends on concentration of substrate and internal resistance. Power outputs are restricted when the substrate concentration crosses a specific level [14]. Likewise, high internal resistance created by proton exchange membrane (PEM) also limits the power output. Therefore, to minimize the effect of internal resistance through removal of PEM, novel configuration of MFC were developed namely single chamber MFC, upflow MFC, and stacked MFC [14]. These novel configurations endure the process of redox reaction by achieving electro neutrality through compensating the transport of electrons from anode to cathode with transport of equal amount of positive charge to cathode. An overview of MFC configuration with anode properties and modification methods is outlined in Fig. 9.1.

## 3. Electrodes and its properties

Electrodes are a key component of any bioelectrochemical system. The type, nature, configuration, and design of electrodes play a crucial role in determining its electrochemical performance and in turn cost of the process. Electrodes can be categorized

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into two types depending the nature of catalyst used as chemical electrodes and bioelectrodes. Any electrode irrespective of its type should possess few basic characteristics of good conduction, mechanical strength, and stability. For a bioelectrode, it should be compatible and possesses a rough surface to facilitate bacterial adhesion. It should also show an ability to transfer electrons between bacteria and electrode [15]. Henceforth, an electrode should possess some basic and specific properties to favor better functioning of MFCs. The specific properties of an electrode material that make them more desirable to be used as an anode in MFCs is discussed below:

1. Electric conductivity: The electrode material possessing high electrical conductivity will enhance the electron flow from anode toward the cathode by an outer electric circuit, which ultimately will increase the quality of the MFCs [16,17]. Recently, researchers [18] used polypyrrole-carboxymethyl cellulose-titanium nitride/carbon brush hydrogel (PPy-CMC-TiN/CB) as a bioanode in MFC. The current density ($3.15\,A\,m^{-2}$) and power density ($14.11\,W\,m^{-3}$) were enhanced by 5.34 and 4.72 times, respectively, as compared to carbon brush anode ($0.59\,A\,m^{-2}$ and $2.99\,W\,m^{-3}$). Enhancement in the current density and power density were partially due to the formation of conducive interface between conductive polymer and substrate after doping titanium nitride in anode. In another study [19], a binder-free manganese cobalt oxide ($MnCo_2O_4$@CF) anode was synthesized using a conventional carbon felt (CF) by a facile hydrothermal method. Low charge transfer resistance ($512\,\Omega$) of $MnCo_2O_4$@CF resulted in high electrocatalytic activity and improved power density ($945\,mW/m^2$), which was 3.8 times higher than CF anode.
2. Surface area and porosity: The surface area of the electrode material will play an essential role by increasing the power output of the MFCs. Increased surface area will possess higher reaction sites and facilitates more electron movements to result in higher efficiency of MFCs. Contrary, high porosity of the material will decrease the electrical conductivity [17]. A study conducted by Gajda and her associates [20] using powdered activated carbon (PAC) modified carbon fiber scaffold as an anode in the ceramic-stacked MFC showed enhanced power density (upto 77%). Microporous structure of PAC favored increased attachment of microorganisms and enhanced power density.
3. Cost and accessibility: The cost of the electrode material is an important factor for the development of the MFCs. Low cost and easy availability play crucial role in the commercialization of fuel cell application. Studies so far suggest that platinum is one of the suitable and widely used component for electrode construction, but its high cost and low availability make it nonsustainable [21]. Hence, composite of the precious metals appear as the better alternative.
4. Stability and durability: The electrode materials are continuously exposed to the oxidation and reduction reaction during the operation of MFCs. So, it is important that an electrode material remains durable and stable irrespective of both acidic and alkaline environment. This would also minimize the cost of maintenance [22]. In a study conducted by Liu and his associates [23], polydopamine decorated reduced oxide graphene (rGO@PDA) on carbon cloth (CC) enhanced

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adhesion between rGO and CC, increased electrochemical stability, and resulted in power density of $988.1 \pm 5.2\,\mathrm{mW\,m^2}$.

5. Biocompatibility: As we know, the oxidation of organic feed in an anodic chamber is carried by bacteria, it is essential that the anode material is compatible with the bacterial culture. Materials like copper, silver, and gold are not considered biocompatible due to their corrosive nature [24]. Moreover, their antibacterial properties inhibit the bacterial growth [25,26]. Graphene anode modified with nontoxic and biodegradable biomolecule extracted from Eucalyptus leaves showed hydrophilicity and increased biocompatibility [27]. Improved surface area of anode possesses high water contact angle (93 degrees) than bare carbon fiber paper (0 degree) and hence helps bacteria like *Escherichia coli* to adhere strongly onto hydrophilic surface to facilitate EET [28,29].
6. Environmentally friendly: The anode material should also be eco-friendly so that it will minimize the carbon footprint during its production.

## 4. Anode modification in MFC

In electrochemistry, anode is a source of electrons and cathode acts as a sink for electrons, i.e., the conventional current in a device flows through anode in external electric circuit to cathode. However, the voltage polarity on anode with reference to cathode depends on device type and mode of operation. In case of device that consumes power, anode is positive, whereas in device that provides power, anode is negative. In electrochemical cell such as MFC, anode is the terminal acceptor of electron that is produced by bacteria. Hence, the redox potential of the anode determines the bacterial activity.

In the anodic chamber of MFC, microorganisms play a vital role as they generate electrons that are utilized to reduce the terminal electron acceptor to produce electric current. The essential prerequisite conditions for the oxidation of organic substrate include the availability of organic-rich substrate, microorganisms, mediators (optional), and anode with excellent properties. The reaction that occurs in the anodic chamber is summarized in Eq. (9.1).

$$\text{Organic matter} \xrightarrow[\text{Anaerobic condition}]{\text{Active microbes}} CO_2 + H^+ + e^- \tag{9.1}$$

To drive the reaction mentioned in (Eq. 9.1), the activation energy must be brought down sufficiently with the help of catalysts. In case of MFC, the anodic biofilm works like the catalysts that boost the reaction [30]. However, the adhesion and enrichment of bacterial biofilm depend on the nature and configuration of anode. As mentioned earlier, an anode addition to the base properties should possess specific properties of surface roughness and microbial compatibility for better bacterial adhesion and electron transfer between anode and bacteria. Although the anode materials used so far supported the bacterial growth and favored electricity generation, improved configurations and surface modifications can accelerate the MFC performance. Till date, a number of anode materials are modified by various techniques

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and agents to improve the performance of MFCs. Surface treatment (physical and chemical), surface coating (electroactive or conductive), and nanocomposite electrodes are the three different types of anode modifications explored till date [15]. The anode modifications and its impact on MFC performance are summarized in Table 9.1 and discussed in the following sections.

## 4.1 Carbon anode and its modifications

In electrochemistry, a wide variety of anode materials have been used, but carbon compounds such as carbon cloth, carbon paste, graphite sheet, carbon brush, graphite rod, graphite felt, activated carbon, and carbon paper are more popularly utilized owing to its impressive characteristics such as biocompatibility with microbial consortia, remarkable specific surface area, high conductivity, and stability in harsh pH conditions. In addition to these features, carbon materials are cost effective thereby increasing its utilization in MFC.

Jung and Regan [59] utilized carbon paper as anode in MFC with glucose as a carbon source and achieved nearly 40 $mW/m^2$ of power generation. Carbon paper as an anode in MFC generated higher power of around 52 $mW/m^2$ using lactate as a substrate [60]. Contrary, when cysteine was used as a substrate, MFC resulted in comparatively lower power output of 36 $mW/m^2$ [61]. It is clearly evident that similar type of anode material showed different power output values, with different substrates indicating dependency of MFC on type and concentration of substrate in addition to other factors. A carbon cloth anode in MFC generated as high as 470 $mW/m^2$ using sodium acetate as a substrate [62]. High-power density using carbon cloth anode is obtained due to higher specific surface area and high porosity of carbon cloth. Unlike carbon paper and carbon cloth, graphite anode in MFC produced very low power output (16 $mW/m^2$) using same substrate [63]. In yet another study, graphite anode in MFC generated still lower power density of 14 $mW/m^2$ using marine sediment mixed acetate substrate [64]. It can be concluded that graphite as an anode material in MFC generates lower power density, which can be associated with lower specific electrode surface area. However, graphite anode with neutral red could generate higher power density of nearly around 152 $mW/m^2$ using sewage sludge in single chamber MFC. Moreover, in addition to surface area of the electrode, mediators also accelerate power generation in MFC.

The unmodified anode material commonly generates lower power density in MFC due to inadequate electrocatalytic activity for anodic microbial reaction therefore anode modification becomes the most pertinent approach for performance enhancement. Platinum is the most popular catalyst in electrochemistry. Even graphite sheet modified with platinum and polyanilineco composite could achieve thousand times more power density (6000 $mW/m^2$) as compared to other type of modified anode materials in MFC using sewage sludge [65]. The utilization of platinum and similar metals is not much attractive because of their higher cost. Therefore, an alternative approach for anode modification such as employing nanomaterials/nanocomposites and other compounds has been studied extensively. Fig. 9.2 depicts the SEM image of bare and modified electrode.

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**Table 9.1** Anode modification in MFC.

| Sr. no | Anode material | Anolyte | Catholyte | Anode modification material | Efficiency | Reference |
|---|---|---|---|---|---|---|
| 1 | Graphite | Marine sediments | Seawater | Microbial oxidants (anthraquinone-1,6- isulfonic acid) | 98 mW/m$^2$ | Lowy et al. [31] |
| 2 | Nickel foam | Glucose solution | – | Carbon nanotube /polyaniline | 42 mW/cm$^2$ | Qiao et al. [32] |
| 3 | Carbon felt | Brewer wastewater | Air/ oxygen | Quinone | 30 mW/cm$^2$ | Scott et al. [33] |
| 4 | Carbon paper | – | – | Polypyrrole-doped carbon nanotube | 228 mW/cm$^2$ | Zou et al. [34] |
| 5 | Graphite rods | Chocolate industry wastewater | Potassium phosphate buffer | Microorganisms | 0.15 mW/m$^2$ | Patil et al. [35] |
| 6 | Carbon | – | – | Polypyrrole/anthraquinone-2,6-disulfonate | 823 mW/cm$^2$ | Feng et al. [36] |
| 7 | Graphite electrodes | Domestic wastewater | Potassium ferricyanide | Aryl diazonium salts | 50 mW/m$^2$ | Picot et al. [37] |
| 8 | Stainless steel mesh | Acetate | Phosphate buffer solution | $Fe_3O_4$ and activated carbon | 809 mW/m$^2$ | Peng et al. [38] |
| 9 | Graphite | – | – | Iron/sulfur | 1.8 W/m$^2$ | Bouabdalaoui et al. [39] |
| 10 | Carbon cloth | – | – | Formic acid | 877 mW/m$^2$ | Liu et al. [40] |
| 11 | Carbon paper | – | – | $Fe_3O_4$/CNT by solvothermal synthesis | 830 mW/m$^2$ | Park et al. [41] |
| 12 | Glassy carbon eectrode | – | – | CNT/$SnO_2$ | 1421 mW/m$^2$ | Mehdinia et al. [42] |

*Continued*

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**Table 9.1** Anode modification in MFC—cont'd

| Sr. no | Anode material | Anolyte | Catholyte | Anode modification material | Efficiency | Reference |
|---|---|---|---|---|---|---|
| 13 | Carbon cloth | Lactate | $K_3[Fe(CN)_6]$ and KCl solution | Tartaric acid-doped polyaniline polymers | 490 mW/m$^2$ | Liao et al. [43] |
| 14 | Nickel foam | Bad wine | Ferricyanide in phosphate buffer | Titanium carbide and chitosan | 18.8 W/m$^3$ | Karthikeyan et al. [44] |
| 15 | Stainless steel mesh | – | – | Carbon black | 1.91 mA/cm$^2$ | Peng et al. [45] |
| 16 | Carbon cloth | – | – | PANI/graphene by In-situ electropolymerisation | 884 ± 96 mW/m$^2$ | Huang et al. [46] |
| 17 | Carbon felt | – | – | Graphene oxide/manganese oxide by dip coating and electrodeposition process | 2065 mW/m$^2$ | Zhang et al. [47] |
| 18 | Activated carbon | – | – | Polydopamine | 803 mW/m$^2$ | Du et al. [48] |
| 19 | Carbon cloth | Phosphate buffer solution (PBS) | PBS and oxygen supply | Brush-like polyaniline | 567 mW/m$^2$ | Zhang et al. [49] |
| 20 | Carbon cloth | Synthetic media | PBS with ferricyanide | Biogenic gold nanoparticles | 178 mW/m$^2$ | Wu et al. [50,51] |
| 21 | Carbon cloth | – | – | Porous nickel oxide/graphene by hydrothermal (solvothermal) synthesis | 3632 mW/m$^2$ | Wu et al. [50,51] |
| 22 | Carbon felt | – | – | NiO/ PANI by in situ electropolymerisation | 1078.8 mW/m$^2$ | Zhong et al. [52] |

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| | | | | | | |
|---|---|---|---|---|---|---|
| 23 | Stainless steel wool | – | – | PANI/polypyrrole by electrochemical polymerization | 2880 $mW/m^2$ | Sonawane et al. [53] |
| 24 | Graphite felt | Potassium ferricyanide | – | Biogas effluent | 1842 $mW/m^3$ | Kamaraj et al. [54] |
| 25 | Carbonc | – | – | $NiWO_4$/rGO by coating | $1128 \pm 42$ $mWm^{-2}$ | Rani and Kumar [55] |
| 26 | Carbon veil fiber | Urine | – | Activated carbon powder | 21.1 $W/m^3$ | Gajda et al. [20] |
| 27 | Carbon felt | – | – | Ru/Fe catalyst by reduction and coating | 600 $mWm^{-2}$ | Qiu et al. [56] |
| 28 | Graphite electrode | Domestic-wastewater | – | Acid and electrochemical surface treatments | 2.0 $A/m^2$ | Roubaud et al. [57] |
| 29 | Carbon cloth | – | – | $I_2$ doped PTh-NP using dip-dry method | 840 $mWm^{-2}$ | Rajendran et al. [58] |

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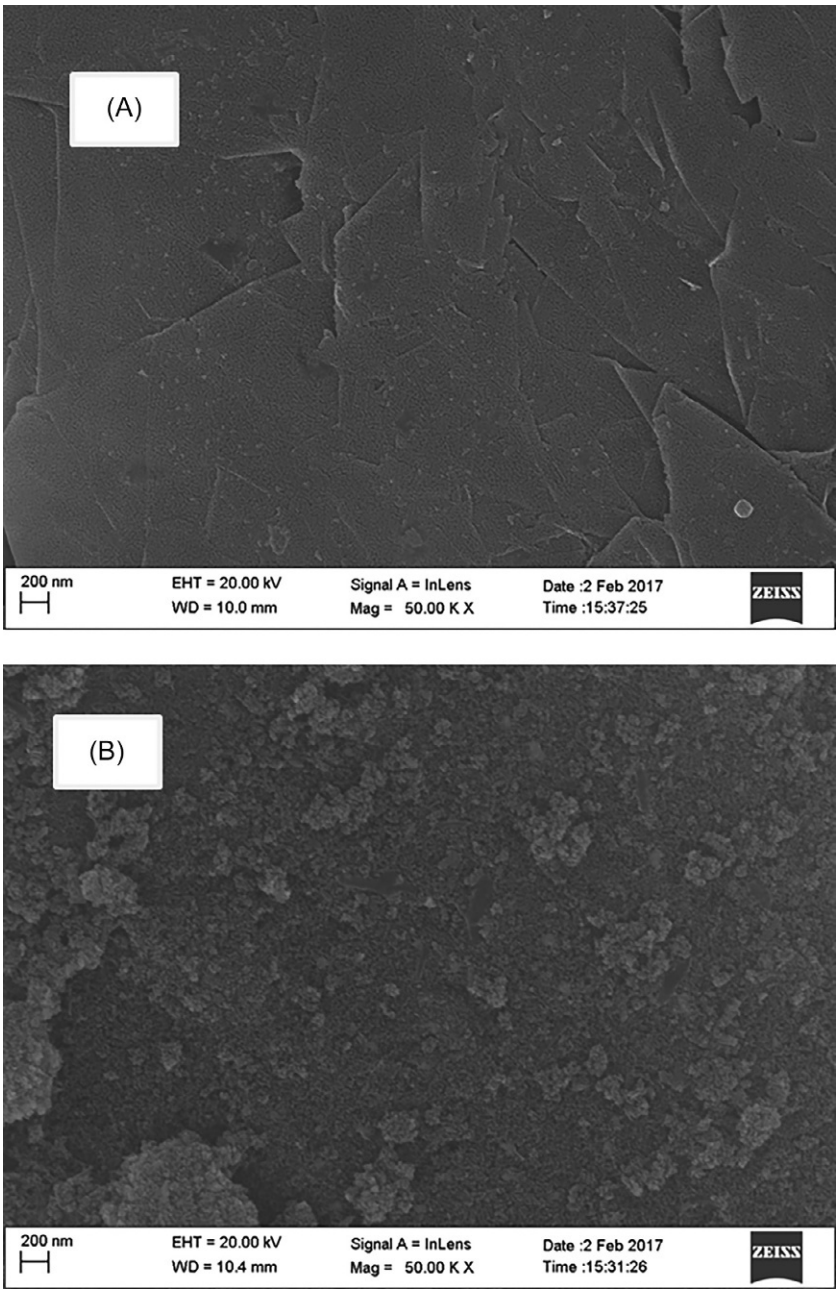


**FIG. 9.2**

(A) SEM image of bare graphite sheet and (B) SEM image of nanoparticle-coated graphite sheet.

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In one of the studies, carbon paper anode modified with polypyrrole-coated carbon nanotubes (CNT) recorded power output of 228 $mW/m^2$ when glucose was used as a substrate [34]. Similarly, a composite prepared out of CNT and polyaniline (PANI) generated around 91 $mW/m^2$ of power density. In one of the studies, MFC operated with bamboo-like nitrogen-doped CNT anode resulted in the generation of 1040 $mW/m^2$ power output using sodium acetate as an organic substrate [62]. Similarly, carbon cloth anode modified with nitrogen-doped carbon nanoparticles produced 298 $mW/m^2$ with sodium lactate as a carbon source [66]. The addition of modifiers on anode invariably increased the specific surface area of the anode with subsequent improvement in the capability of charge transfer. This led to the significant enhancement of electrochemical activity for the anodic reaction.

## 4.2 Pt anode in MFC

Platinum is one of the extensively used and efficient electrocatalyst for fuel cells [67,68]. But being an expensive metal, it possesses major drawback in fabrication and application of MFCs [67]. Researchers across the globe are trying to overcome this disadvantage by enhancing catalytical activity through minimized loading of Pt in combination with other precious metals [69]. In a study, Park et al. [70] incorporated highly dispersed Pt-black and Pt nanoparticles on carbon paper by using an e-beam evaporator. Pt loading with thickness ranging from 3000 to 4000 Å leads to an increase in the current density (0.42 $A/m^2$) by two times as compared to *E*-Tek commercial anode.

One of the interesting studies conducted by Moreira et al. [71] showed that boron-doped diamond (BDD) and Pt anodes developed by photoelectro-Fenton (PEF) process showed comparatively faster trimethoprim (TMP) degradation as compared to electrodes prepared by solar photoelectro-Fenton (SPEF) process. PEF-BDD showed better performance than PEF-Pt. Contrary, in SPEF, the influence of the anode was almost negligible. A similar study was conducted by Saha et al. [72] where β-$Mo_2C$ hollow nanotubes were modified with Pt NPs via atomic layer deposition (ALD). This modification showed 111% higher power density (414 $mW\,cm^{-2}$) and 20% better activity and durability than commercially available Pt/C anode.

## 4.3 Nickel anode and its modifications in MFC

Nickel electrodes are another type of electrode in popular use in MFC operation. In a study, Modi et al. [73] reported that electrode modified by in situ doping of nitrogen on nickel nanoparticle dispersed carbon nanofibers using catalytic chemical vapor deposition showed twofolds enhanced power density upto $1850 \pm 20$ $mW/m^2$ as compared to nitrogen-undoped electrode. Moreover, it also increased the electrode material conductivity and provided favorable condition for the bacterial growth. Likewise, in a study conducted by Mardanpour and Yaghmaei [74] in fabricated microfluidic MFC operated with nickel electrodes showed maximum power density upto 104 and 14 $W\,m^{-3}$ when operated with nutrient broth and glucose, respectively.

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Mousavi et al. [75] reported volumetric power density of upto 343 $W m^{-3}$ in microfluidic MFC operated with nanostructured nickel-based anode.

Nickel was also used in combinations with other metals in the past few years. In a study conducted by Li et al. [76], graphene-cobalt/nickel composite-carbon cloth (Gr-Co/Ni-CC) electrode prepared by dip-coating method was used in MFC. Results of the study showed reduction in the internal resistance by upto 158.52 Ω with maximum power density of 785 $mW m^{-2}$. Similarly, Zhu et al. [77] used graphene-modified nickel-based anode prepared using electrodeposition (ED) method in MFCs. This modification improved EET efficiency of anode and reduced the charge transfer resistance (Rct) by 98% as compared to bare Ni anode. It resulted in maximum power density that was 26 times higher (468 $mW m^{-2}$) than bare Ni anode (18 $mW m^{-2}$).

## 4.4 Conductive polymer for anode modification in MFC

Conductive polymers are known to possess good conductivity and durability and hence popularly utilized as doping agents for anode materials. The added benefits of conductive polymers are that it provides better bacterial cell adhesion to the electrode surface. Some of the prominent conductive polymers used in MFC for anode modification include polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), and hydrogels. In one of the studies, when polyaniline nanocomposites were electrochemically polymerized on the graphite felt electrode, the initial startup time of MFC reduced relatively due to the better bacterial attachment on the anode and enhanced electrochemical activity of bacteria [78]. According to Cui et al. [79], bacterial attachment has also been reported to be plausible reason behind high conductivity. Increased surface area for bacterial attachment and improved electrochemical activity improved the performance of carbon nanotube modified polyaniline nanocomposites/graphite felt anode [79]. The polyaniline nanocomposites increase the hydrophilicity of graphite felt electrode and thus improved the electrostatic interaction with the negatively charged bacterial cells. Polyaniline nanocomposites are cost effective, biocompatible, and can be easily synthesized, but its electron transfer capability, durability, and its stability are easily hampered by its shrink-swell tendency when deposited on the electrode [80]. Therefore, to eliminate this limitation, a composite of polyaniline was prepared with reduced graphene oxide and platinum (Pt) using in situ polymerization and reduction method. When this composite was deposited on the carbon cloth electrode, the current density was found to improve remarkably in MFC over longer operational time. It is attributed to the fact that Pt formed covalent bond with the nitrogen moiety of the polyaniline, hence preventing agglomeration of Pt and restricting swelling of polyaniline. In addition, during longer operation time, restacking of reduced graphene oxide was observed along with increased catalytic active sites, high current density, and low ohmic resistance [81].

Polypyrrole is another electrically conductive polymer with environmental friendly nature, but its chemical structure is yet not defined well because it possess

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major amount of α-β linkage on its polymeric side chain that causes structural disorientation restricting electrochemical response [82]. Polypyrrole was doped with reduced graphene oxide and used to modify carbon paper electrode in MFC. The power density in the modified carbon paper was found to be three times higher than that of unmodified carbon paper electrode because of increased efficiency of charge transfer achieved through improved available total surface area causing high contact angle between the anode surface and bacterial cell adhesion [83]. Poly (3,4-ethylenedioxythiophene), another conductive polymer also termed PEDOT, has been used to modify graphite felt electrode. PEDOT showed better performance because of its 3D architecture (66). When PEDOT was electrochemically deposited on carbon cloth electrode in MFC, 43% increase in power density was recorded in the modified electrode because PEDOT increased redox active centers and decreased the anodic resistance of the anode [40]. The electrically conductive polymers have also been coupled with nanoparticles to form hydrogel. Hydrogel consists of complex arrangement of swollen polymers in water. In one of the studies, the carbon nanotube (CNT) was doped with hydrogel and used to modify the carbon paper electrode via electrodeposition where $H^+$ ions were reduced to $H_2$ in the colloidal solution of CNT when −3 V of potential was applied. The modified electrode showed better MFC performance largely due to increased proximity between anode and bacterial cell wall [40].

## 4.5 Chemical anodic modifiers in MFC

When certain functional groups are coated on the surface of the anode, microbial attachment to the anode is improved and EET is facilitated. The chemical modification done using electrochemical oxidation requires short treatment time and ambient temperature [84]. The carbon cloth anode has been chemically modified using specific electrodes such as nitric acid ($HNO_3$)/sulfuric acid ($H_2SO_4$), ammonium nitrate ($NH_4NO_3$), and diazanium sulfate $(NH_4)_2SO_4$ with the help of electrolysis. The modification provided increased electrochemically available surface area in the anode resulting in quick start up time [84,89]. However, during prolonged MFC operation, the electrochemical activity of bacteria was found to diminish due to reduced metabolism of bacteria attached to the anode [84]. According to Liu et al. [40], 5% ammonium carbonate used to chemically modify the carbon cloth anode using electrochemical oxidation increased the number of amide functional groups attached to the surface of the anode, resulting in increased current density. In yet another study, carbon cloth anode was modified by immersing it in a solution of formic acid. The formic acid exfoliated the oxygen and the nitrogen moieties from the surface of the anode that facilitated adherence of thicker bacterial population causing increased power output [40,90]. Ethylenediamine and nitric acid were tested for modification of activated carbon fiber felt anode. The amide functional groups introduced by ethylenediamine facilitated increased bacterial attachment to the anode and eased the transfer of electrons as compared to oxygen

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functional groups introduced by nitric acid. The start up time in MFC was significantly reduced in both the modification methods. However, the amide functionalities were observed to be more biocompatible when compared to oxygen functional groups [85].

## 4.6 Anode modification using metal oxide nanocomposites

Oxides of certain metals such as tin (Sn), titanium (Ti), and iron (Fe) have been used to modify anode in MFC to improve EET. Tin oxide is found abundantly in nature and is structurally stable, conductive and economical. It has been used as an anode modifier in MFC because of its unique physical and chemical properties. Multiwalled CNT was composited with $SnO_2$ and utilized to modify glass carbon anode. The modified electrode enhanced the performance of MFC as compared to plain glass carbon anode [42]. In one of the studies, $SnO_2$ was grafted on reduced graphene oxide via microwave dispersion mediated by hydrothermal method and used as modifier for carbon cloth electrode. The power density recorded with modified anode was 4.8 times more compared to the plain carbon cloth anode [42]. It was shown in one of the studies that indium tin oxide was modified with graphene nanosheets and poly(allylamine hydrochloride) using multilayer self-assembly technique. It improved the conductivity and adhesion of bacteria over the anode resulting in the increased performance of MFC.

The practical application of titanium oxide as anode in MFC is encouraging because of its chemical stability and biocompatibility. The vertically aligned $TiO_2$ nanotubes on carbon paper formed 3D vertical infiltrating pores that offered huge accessible surface area for direct electron transfer and biocompatibility facilitating easy molecular diffusion and improving overall performance of MFC [86]. Titanium dioxide was doped with egg albumin and used as composite to modify loofah sponge carbon to form a 3D anode. MFC operated with modified anode recorded improved capacitance due to synergistic effects of modifier ($TiO_2$) and carbon from egg white. Egg white provided an ideal surface formation for easy exchange of bacterial electron for redox reaction [87,88]. Iron oxides such as hematite ($Fe_2O_3$), magnetite ($Fe_3O_4$), and goethite (FeO(OH)) are usually utilized as anode modifiers in MFC to achieve improved power output. The $Fe_2O_3$ was used to modify carbon cloth via pyrolysis ferrocene and used in MFC [82]. This modification enhanced EET efficiency of the bacteria resulting in six times higher current density production when compared to plain carbon cloth. The $Fe_3O_4$ was integrated with CNT through synthetic solvothermal method, and this composite was used to modify carbon paper anode to operate in mediatorless MFC. The magnetic attraction brought about by magnetite enhanced the CNT attachment to the anode thereby rendering the CNT to offer favorable nanostructure surface for the growth of bacteria [41]. In another study, a composite was prepared from goethite and activated carbon to modify stainless steel. This modified anode served as current collector and produced 36% more power density as compared to unmodified anode [38].

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## 5. Conclusion

The anode in an MFC happens to be the principal component as it governs the power generation. With an intention to develop high-performance MFC, the anode modification is focused much. The anode modification mainly aims to achieve efficient wastewater treatment by extracting net positive energy output and to harvest it. Nanomaterials have shown to be potential anodic modifiers, but they exhibit remarkable efficiency only when utilized as composites indicating synergistic roles of each component. Also, anode modification using specific functional groups through electrochemical oxidation gave promising results, but electrochemical modification of anode for large-scale MFC application is still questionable due to time intensiveness, high cost of the materials, and intricate steps involved during the reaction, which in turn limits the large-scale practical application. Sometimes the chemicals involved in the electrochemical process of electrode modification can be detrimental for the environment. Therefore, further research needs to be done to incorporate environment friendly organic/inorganic compounds for electrochemical oxidation of anode. Moreover, biocompatible conductive polymers that are derived from the microorganisms should be encouraged.

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CHAPTER

# 10 Influence of operational parameters on the performance of microbial fuel cells

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## 1. Introduction

High energy demand and growing need of potable water are global concerns with ever increasing population and industrialization. It is predicted that by 2030, the total urban population will be around 5 billion. Hence, it is necessary to discover cost-effective and sustainable technology to meet global demands concerned with energy and water needs [1]. Recently developed microbial fuel cell (MFC) has the capability of simultaneous decontamination of wastewater and power production. An environment-friendly mode of operation of the MFCs to produce power from organic wastes through their oxygen reduction reaction has fascinated researchers to study the efficiency of various types of MFCs for large-scale application. Logan in one of his studies predicted that if waste produced by the population of 1 lakh people ($16.4 \times 106$ L/year) is utilized for producing power, it could probably run 2.3 mW wastewater plants [2]. A typical structure of a MFC constitutes a cathode and anode well segregated using an ion exchange membrane (IEM)/separator. The hydrogen ions are liberated in the anodic chamber using the organic substrate. These ions are then transferred to the cathodic chamber. These ions are then accepted by oxygen receptors at cathode to generate energy. Such types of cells are known as bio-electrochemically assisted microbial reactors [3].

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MFCs provide benefits over many traditionally used fuel cells like enzymatic fuel cells. Potential of microbes to metabolize organic substrates directly facilitates high energy conversion potential. However, commercialization of MFCs on a large scale is restricted due to several disadvantages of electrode and separator materials used in the process. This review paper gives brief information about various physical, biological, and chemical factors influencing the proper working of the MFC. It also summarizes the efficiencies of different types of configuration of MFCs like single-chambered MFCs, double-chambered MFCs, and upflow MFCs. A brief analysis of the challenges and future prospects related to MFCs are also described.

## 2. Physical parameters influencing the performance of MFCs

MFC is a bioelectrochemical unit that typically comprises a bioanode and biocathode compartment with an IEM separating them. The performance of MFCs in the treatment of wastewater and the generation of energy is highly dependent on certain physical parameters such as appropriate electrode material, surface area of the electrodes employed in the process, configuration of MFC reactor, and type of IEMs. Large number of experiments are carried out to elevate the efficiency of MFCs by improving the physical parameters concerning electrodes and IEMs used in MFCs.

### 2.1 MFC reactor components

#### *2.1.1 Electrode material*

The applicability and economic viability of MFCs in energy generation and wastewater treatment are primarily allied with development in electrodes material used in the process.

##### Anode

The construction of an optimum anode is a significant approach to broaden the potential application of MFCs in the practical world. A remarkable development was observed in the past few decades to design highly effective anode electrodes for MFCs [4]. An ideal anode material should possess certain characteristics including large biocompatibility, higher mechanical strength, and chemical stability. The anode should be a good conductor of electricity with minimum electrical resistance. For long durability and sustainability of the anode, the material used should be noncorrosive and robust [5]. The substances used as anode in MFCs are described below.

***Carbon-based anodes.*** Anodes based on carbon are preferred in the MFCs because of its sustainability, cost-effectiveness, great biocompatibility, and electrical conductivity. Additionally, a wide range of morphological structures of carbon facilitate the engineering of the most efficient anode. For the construction of anode, a variety of carbon materials are applied ranging from highly distinct graphite carbon to carbonaceous materials [6].

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***Graphite.*** The crystalline form of carbon, namely graphite, acts as an excellent material for manufacturing of anode used in MFCs. Due to its $sp^2$ hybridization structure, graphite is highly stable and acts as an excellent conductor of electricity. Graphite anode is constructed in different organizations like plane arrangement, a packed arrangement, a brush like arrangement, or felts or foam arrangement. A comparative study was conducted using a rod-shaped graphite and felt graphite by taking *Rhodoferax ferrireducens* as an inoculum. It was observed that relatively higher electricity was produced when graphite felt was used as the anode owing to its high surface area in contrast to graphite rod [7]. Shortly, a brush structured graphite was constructed that efficiently increased the electricity production by reducing the internal resistance in MFCs system [8]. Further, the performance of plane structured graphite was evaluated against felt graphite, and its result indicated that plane graphite generated double the energy than felt graphite [9]. It was also observed that the incorporation of metallic substances into graphite increased the efficiency of the anode in MFCs. In one of the studies, anode graphite was doped with calcium sulfide. The results of the studies suggested that the energy generation was enhanced with increasing bacterial affinity toward the doped graphite anode [10].

***Carbon cloth, meshes, paper, and associated materials.*** Carbon-associated materials like carbon cloth, mashes, paper electrodes, carbon foam, and carbon felt are nowadays used on a large scale in MFCs. In recent times, paper electrodes made up of carbon allowed the formation of biofilms by facilitating the attachment of bacteria on its porous surface and thus increasing the electricity generation [11]. Vast amount of research concluded that the hydrophobic nature and nonporous morphology of the carbon felt and carbon cloth prevented biofilm formation at the surface of the anode, ultimately reducing the power generation capability of MFCs. Thus, pretreatment of such carbon-associated anode material is necessary in order to enhance its efficiency. In one of the studies, carbon felt anode was partially oxidized using ultraviolet/ozone treatment to reduce the hydrophobic nature of the carbon felt and increase its porosity [12]. Further, the carbon felt was also treated with nitric acid to decrease the resistance provided by anode and thus improving MFC performance [13]. In 2009, carbon mesh and carbon paper were treated with heat in order to eliminate the impurity present on anode [14]. The treatment of carbon-associated anode materials using $H_2O_2$, NaOCl, or isopropanol also enhanced the energy production in MFCs [15]. In 2013, Guo along with his coworkers studied the effect of surface charge and hydrophilic nature of anode on the production of energy in MFCs. As most of the bacterial cells possess negative charge, introducing positive charge on the surface of the anode facilitates biofilm formation and thus increases the performance of MFCs [16].

***Addition of carbonaceous material to the carbon anode.*** Most of the studies suggested that the addition of carbonaceous material like activated carbon, carbon nanoparticles, or carbon black to the anode increases the efficiency of MFCs by enhancing the attachment of microbes to the anode surface. In 2014, You and his associates layered carbon cloth/carbon mesh anode with carbon black. The result of the experiment illustrated that the energy generation was almost doubled

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($60.7\,mW\,m^{-2}$) after the pretreatment of anode with carbon black [17]. In another experiment, Suqi Zheng and his coworkers, experimentally proved that coating of stainless steel anode with carbon black enhanced the interaction between microorganisms and anode which further improved the efficiency of MFC [18].

***Carbon nanotubes.*** Use of carbon nanotubes as anode increases the efficiency of MFCs for power generation by significantly increasing the surface area-to-volume ratio and elevating the adherence of bacteria to the anode. In 2015, Hao Ren along with his colleague performed a comparative analysis of differently aligned carbon nanotubes including spin-spray layer by layer carbon nanotubes, randomly aligned carbon nanotubes, and vertically aligned carbon nanotubes as an anode in MFCs. The result of this study suggested the use of spin-spray layer by layer carbon nanotubes extensively for energy generation [19]. Coating of carbon nanbotubes was carried out using a wide range of polymers including chitosans, polyaniline, etc. to increase the roughness, robustness, and adhesive characteristics of the membrane [20,21].

***Metal-based/noncarbon anodes.*** Extensive research was conducted for the determination of the efficiency of noncarbon anodes in MFCs. Stainless steel is a favorable material for anode on account of its remarkable characteristics like mechanical and chemical stability, noncorrosiveness, and high conductivity. However, nonmodified stainless steel is not recommended due to its low efficiency to produce current. For instance, in 2017, stainless steel was used as an anode in an experiment, and it was concluded that highest power production by MFCs was very low ($\sim 4\,mW\,m^{-2}$) [22]. Alteration or treatment of stainless steel surface by thermal treatment or implantation of polymer or carbon material onto SS surface can significantly increase power generation in MFCs. The study by Liang et al. suggested better performance of modified stainless steel than plain stainless steel anode [23].

Ceramic-based anodes are an excellent alternative to most carbon-based anodes used in MFCs due to its potential of high energy generation, electrical conductivity, and robustness in extreme environments. Diego et al. engineered titanium-based ceramic anode and used *Geobacter sulfurreducens* as inoculum which yielded $128.7\,A/m^2$ power [24].

When titanium was used as an electrode, it was costly, unstable and found to be least efficient [25]. Hanno Ritcher and his co-workers employed highly conductive gold as anode and *G. sulfurreducens* were used as an inoculum. It was observed that a constant power of 0.4–0.7 mA was generated. However, use of gold is constrained because of its expensive nature [26].

## Cathode

Like anode, cathode is another essential part of the MFC system. Higher efficiency of cathode in MFCs is very essential for significant power production. It is observed that the use of inappropriate cathode material leads to slow rate of redox reaction of the substrate at cathode surface. This ultimately reduces the efficiency for MFCs of energy generation. During degeneration of organic substrates, electrons produced move toward the anode to ultimately undergo oxidation by electron acceptors at the cathode [27]. Large number of researches of MFCs primarily focuses on substrate

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studies or alteration of anodes. Very less attention is drawn on cathodic electron acceptors, despite the fact that they represent one of the critical parameters that may influence the efficiency of MFCs. For this purpose, research on cathode materials and their modification with suitable substances to enhance the production of energy is the major challenge of time. Additionally, an ideal cathode must be robust, mechanically and chemically stable, and should have catalytic characteristics. Types of cathode used in MFCs are generally categorized as biotic cathodes and abiotic cathodes.

***Abiotic cathodes.*** Abiotic cathodes generally facilitate the reduction of oxygen to generate water. This reaction is usually carried out in the presence of a catalyst or catholyte. Oxygen reduction on cathode surfaces are divided into 2 categories based on the pH and oxygen concentration in the reaction system. The four-electron pathway produces water by complete reduction of oxygen (as shown in Eq. 10.1), whereas incomplete reduction of oxygen by two-electron pathway results in the liberation of $H_2O_2$ [28].

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \left(E^0 = 0.816\,V\right) \tag{10.1}$$

$$2O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_2 \left(E^0 = 0.295\,V\right) \tag{10.2}$$

Carbon cathode impregnated with platinum is considered to be the most optimum cathode that is generally used to reduce oxygen to water. However, poisoning of the catalyst during the reaction and high prices of platinum restricts its use on large-scale energy production. A study was conducted to find replacement for the costly platinum fabricated electrode with some cost-effective electrodes including $Fe_2O_3$, $Mn_2O_3$, and heteroatom-doped carbon [29]. The catalyst poisoning at cathode can be prevented if ferricyanide is chosen as catholyte. Ferricyanide use is not suggested for sustainable processes.

***Biotic cathodes (biocathodes).*** Use of abiotic cathodes in an extensive-scale MFCs system portrays a large number of disadvantages like catalyst poisoning and reduced mechanical and chemical stability. Moreover, platinum-incorporated cathodes require higher concentration of dissolved oxygen ($\sim$2.2 mg/L), which may be toxic for many of the aerobic bacterial reactions. Large amount of research demonstrated that some of the aerobic microorganisms imitate abiotic cathodes and reduce oxygen to water by generating biofilm on the cathode surface [30]. The remarkable advantages of bicathodes over abiotic cathodes are high stability, faster formation of biofilm, self-sustainability, and survival in harsh wastewater conditions. In 2013, Jae Jang along with his co-workers compared performance and stability of MFCs by using both biotic and abiotic cathodes for a period of $\sim$8 weeks. The result of the experiment suggested that power production was maximum when a biotic cathode was used in the MFCs system. Further, the efficiency of the biotic and abiotic cathode was examined by the addition of azide catholyte. Addition of catholyte to the biocathode eventually decreased the power generation, whereas performance of abiotic cathode was unaffected [31]. In another study, activated carbon was used as a

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biocathode in MFCs for treating water contaminated with dyes. The granular-activated biocathode demonstrated high retrieval of dye as well as high energy production in the MFC system [32]. For aerobic cathodes oxygen acts as the ultimate electron acceptor. In such cases, iron or manganese undergo reduction reaction at cathode surface and further they are again oxidized by microbes. Conversely, in case of anaerobic cathodes, the ultimate electron acceptor is directly reduced through microbial metabolism, i.e., in anaerobic condition, other chemicals like sulfate and nitrate act as electron acceptors at biocathode with sulfur-reducing bacteria and denitrifying bacteria, respectively [33].

***Cathode catalyst.*** During the process of energy generation in MFCs, microorganisms present in wastewater cause release of electrons by catalytic breakdown of organic substances present in anode chamber. These electrons are taken up by oxygen present in the catalytic atmosphere of the cathode chamber and cause its reduction to form water molecules. For the proper oxygen reduction reaction, an ORR (oxygen reduction reaction) catalyst is used. A good ORR catalyst should be robust, resistant to mechanically and chemically harsh environments, active, and it should have low cost [34].

Cathode catalysts are categorized into two types namely, platinum-based ORR catalyst and carbon-based/platinum-free ORR catalyst. Most of the lab-scale studies employ platinum-based catalysts on activated carbon cathode in MFCs setup for power generation. Most of the researchers found that impregnation of carbon-based cathode with platinum results in the increase of energy output which is manifold higher than the pure carbon-based cathode. However, disadvantages of platinum-based catalyst such as shortage, catalyst poisoning, and high price of platinum restricts its use on large-scale energy production [35]. Wide ranges of platinum-based bimetallic catalysts were evaluated for enhancing the performance of MFCs. Further, the activity of bimetallic catalyst was compared with platinum-based carbon cathode. Table 10.1 illustrates efficiencies of some bimetallic catalysts in MFCs.

Studies have been conducted to find cost-effective catalysts that can be a better replacement for platinum-based catalysts. Carbon-based catalyst is nonexpensive, highly stable, highly conductive, and provides large surface area for oxygen reduction reaction.

### 2.1.2 Separators in microbial fuel cells

Separator is one of the most significant elements of MFCs that affect the overall efficacy of the power generation in the MFC system. The separator is mainly used as a physical barrier in between the electrodes by preventing diffusion of oxygen in the anode compartment, however, allowing the electrochemical interaction between the two electrodes. An archetypal separator should have properties like superior electrical conductivity, chemical and mechanical stability, robustness, and it should be chemically inert [41]. It also insulates the electrodes thus inhibiting short circuits in the MFCs system. The consumption of protons is generally higher at cathode surface as compared to the transfer of protons through the separator. Thus, it is crucial to employ separators featuring high cation exchange characteristics. In MFCs, catalytic

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**Table 10.1** Efficiencies of some bimetallic catalysts in MFCs.

| Type of MFC | Type of cathode used | Type of bimetallic catalyst | Power output/ power density | Reference |
|---|---|---|---|---|
| Single-chambered air cathode MFC | Carbon cloths | Pt-Ni alloy catalysts | $1724\,mW\,m^{-2}$ | [36] |
| Air-cathode single-chamber cylindrical MFCs | Carbon cloth | PtCo/G catalyst | $1378\,mW\,m^{-2}$ | [37] |
| Membrane-free cylindrical single-chamber air cathode MFC | Carbon cloths | Platinum-iron/ carbon-based binary alloy electrocatalysts | $1680 \pm 15\,mW\,m^2$ | [38] |
| Air breathing MFC | Cathodes fabricated with stainless steel wire mesh | $Ag_3Pt$ bimetallic catalyst | $999\,mW/m^2$ | [39] |
| A dual-chambered MFC | Air-cathode consisting of stainless steel mesh current collector | Fe-Mn bimetallic nanocatalysts | $1940 \pm 31\,mW\,m^2$ | [40] |

breakdown of substrates occurs in anodic chamber, leading to the production of electrons at anode surface. Further, the produced electrons are communicated to the cathode via an external circuit, whereas protons are exchanged from anode to cathode compartment via a separator. However, use of single-chambered MFC that lacks the separator decreases Coulombic efficiency (CE) by increasing the oxygen and substrate diffusion between anode and cathode compartments [42].

Biofouling constitutes the dominating issue for membrane biological reactors. MFCs as well as other bioreactors, for example, layer bioreactors applied for wastewater treatment and membranes employed in microbial desalination cells experience the ill effects of biofouling over the long haul. Biofouling leads to the reduction in the power production by decreasing hydrogen ion transport through the membrane. Many researchers have reported the disadvantages of using the separators in MFCs. One of the important setbacks of using separators is pH splitting, in which subsequent

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reduction of pH in anode chamber and rise of pH in cathode chamber were observed. This eventually decreases the stability and efficiency of MFCs. This also leads to amplified internal resistance of the system. The separators are basically divided into three groups on the basis of their filtration characteristics; size-selective separators, IEMs, and salt bridge [43].

### Ion exchange membranes (IEMs)

***Cation exchange membrane (CEM).*** In the past few decades, CEMs are used on a large scale for separation of cations, especially protons across the membrane in MFCs. One of the commercially used CEMs is Nafion, which was manufactured by DuPont Inc., USA. It is a perfluorosulfonic acid membrane that comprises fluorocarbon backbone with sulfonate group linked to it. Negative charge of the sulfonate group provides excellent conductivity to different cations [44]. Another polymer-based CEM namely Ultrex CMI 7000 demonstrated higher mechanical and chemical stability and sustainability when compared to Nafion. Large number of sulfonic acid groups linked to polystyrene and divinylbenzene cross-link gel provided an excellent conductivity to the CMI 7000 membrane [45]. In 2006, Solvay-Solexis, Italy developed a short-chain perfluoro-polymer membrane named Hyflon that exhibited enhanced conductivity and sustainability as compared to Nafion membrane but offered internal resistance in MFCs system, which ultimately decreased overall performance of MFCs [46]. Shortly, another commercial CEM was developed named Zifron which offered minimum internal resistance in MFCs. Zifron was basically made up of macroporous organic minerals that consist of zirconium dioxide and polysulfone [47].

CEM provides competitive exchange of different cations besides protons, which results in pH splitting. Also, durability and sustainability are significantly reduced by the subsequent formation of biofilm on CEM. High cost and biofouling of the CEM constrain the application of CEM on large.

***Anion exchange membrane (AEM).*** As CEMs were not efficient enough to transport less concentration of protons across the membrane, studies were carried out to find a better substitute for CEM. An anion exchange membrane demonstrated its potential of transfer of protons using carbonates or phosphate as proton transfer and pH buffer. Using anion exchange membranes in MFCs also helped in overcoming the problem of pH splitting by maintaining pH balance in the MFC system. Kim along with co-workers executed comparative analysis of CEM and AEM membrane. It was observed that when AEM was employed in MFCs, energy generated was $\sim 0.61\,W\,m^2$ and for CEM it was $0.48\,W\,m^2$ [48]. In another study, anion exchange membrane was used in membrane cathode assembly, where it generated energy of $13.1\,W\,m^3$, which was much higher than the energy obtained using CEM-based cathode assembly [49].

Use of anion exchange membrane in MFCs has several disadvantages. For instance, AEM is highly permeable for the substrates used and are more likely to get deformed away from cathode in case of single-chambered MFCs. This sort of deformation may produce an empty space between the cathode and AEM, which

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ultimately increases the internal resistance. Additionally, use of phosphate buffers in AEM increases the cost of the process. However, phosphate buffer can be substituted by bicarbonate buffer that has the same efficiency as that of phosphate buffer and has comparatively low cost [50]. Hence, further research is necessary to solve the problems that arise from the limitations of AEM to facilitate its large-scale application.

***Bipolar membranes (BPMs).*** Recent development of bipolar membranes offers simultaneous exchange of protons as well as hydroxide ions generated via splitting of water across the membrane. A typical BPM is made up of two monopolar membranes namely cation and anion exchange membrane. Due to its bipolar nature, BPMs can transport both negatively and positively charged ions across the membrane simultaneously [51]. Proton transport potential of bipolar membranes is comparatively lower to that of AEM and CEM. However, the use of BPM is suggested in desalination of wastewater due to its potential to transfer ionic species into electrode chambers [52].

***Size-selective separators.*** Non selectivity of IEMs causes pH splitting during energy production in MFCs. In contrast to IEMs, size-selective separators have larger pore size that aids the easy transfer of protons across the membrane and thus increases the efficiency of MFCs. Size-selective separators basically have two types: microporous filtration membranes and course-pore filtration membranes.

Microporous filtration membranes segregate the solutions in cathode and anode compartments, this allows efficient transfer of charged or uncharged species across the membrane. This allows appropriate transfer of protons when favorable pore size of the membrane is selected [8]. In an experiment, ultrafiltration filtration membrane was fabricated with a catalytic sheet and conductive sheet in a tube-like configuration. The energy output of the MFCs was found to be $17.7\,W\,m^3$, which was approximately three times higher than that with CEM [53]. Course-pore filters are cost effective and can be potentially used for large-scale production of energies using MFCs. However, large pore size of course-pore filters may interrupt the biofilm generation by reducing oxygen diffusion across the membrane [54]. J-cloth and canvas substantially transferred protons and generated a large amount of energy. Low cost of course-pore filters facilitate its application on industrial scales. Other examples of course-pore filters are fabrics, glass fiber, nylon mesh, cellulose filters, etc. [55].

***Ceramic-based separator.*** Nowadays, ceramic-based separators are employed in MFCs extensively due to remarkable features like superior permeability and ability to provide insulation to avoid short circuits. Ceramic separator was primarily developed by Park in a double-chambered MFC. Several attempts are made to decrease the price of the ceramic-based membrane in MFCs. In 2010, Behera along with his colleagues introduced earthen pot-dual-chambered MFC in which earthen pot played the role of separator as well as cathode electrode [56]. The surface of ceramic membrane acts helps in the exchange of cation with minimal internal resistance. The mechanical and chemical stability and porous nature of the membrane make this separator a better candidate for MFCs.

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***Salt bridge.*** Salt bridge is a type of MFC separator in which ionic species are transported in a two-chambered MFC system through a glass cylinder loaded with an electrolytic substance. The generally used electrolytes in salt bridge separators are phosphate buffer solution and potassium chloride solution. Mixing of the fluids in salt bridges is prevented by the addition of agar to the electrolyte. A salt bridge separator was engineered by inserting potassium chloride solution and agar (1:5) between two perforate glasswares [57]. In contrast to Nafion membrane, salt bridge is cost-effective, highly sustainable, and exhibits negligible diffusion of oxygen. However, salt bridges have very high internal resistance and produce lower energy. For instance, in 2005, Min and his co-workers proved that salt-bridge offered more internal resistance than Nafion separator in the same operational conditions. Further, the efficiency of potassium chloride-salt bridge was compared against CEM. It was observed that voltage produced by CEM was much higher than that of KCl salt bridge [58].

Since the electrical conductance of salt bridge separators is highly related to the type, concentration, and volume of electrolyte, the reduction in internal resistance can be obtained by employing appropriate concentration of electrolyte into the separator. Energy production in MFCs encompassing salt-bridge separators is further increased by expanding the surface space of salt bridges exposed to the anode and cathode compartments [59].

### 2.1.3 Microbial fuel cells reactor arrangement

Large number of experiments are carried out to enhance the components of MFCs to secure high power production and to improve the working of MFCs in wastewater treatment. Similarly, researchers are making efforts to engineer the most appropriate MFC with suitable configuration to obtain high yield. The design of reactors used in MFCs directly affects its energy yield and Coulombic efficiency. Initially, double-chambered MFCs were used on a large scale. Due to the drawbacks of separators used in MFCs such as biofouling and pH splitting, single-chambered MFCs were introduced. Nowadays, stackable MFCs with serial and parallel configurations are used on a large scale for efficient energy generation. MFCs are categorized on the basis of their configuration and mode of operation. Different types of MFCs are described below.

#### Double-chambered MFCs

A double-chambered MFC is a simple assembly that typically comprises anode compartment and cathode compartment that are well segregated using a separator. Generally, two-chamber MFC encompasses a defined substrate medium in anodic compartment and catholytic solution in cathode compartment. The separator in the MFCs facilitates the exchange of ions and thus energy is generated through batch or continuous mode, as shown in Fig. 10.1.

An experiment was conducted to generate energy in remote areas using two-chambered air-cathode MFC, where oxygen was utilized as an ultimate electron acceptor at cathode surface [60]. H-type dual-chambered MFCs were applied for

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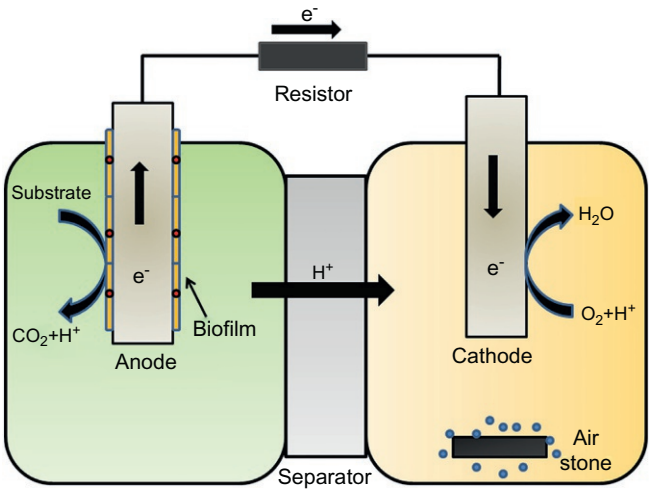


**FIG. 10.1**

Illustration of typical double-chambered MFCs.

energy production using MFCs. However, use of H-type MFCs on an industrial scale is restricted due to its large internal resistance [61]. Further, upflow dual-chambered MFCs were introduced for wastewater treatment and energy production; however, input energy required for pumping fluid into the system was much higher than the energy output. Miniature dual-chambered MFCs with whole surface area of $2\,cm^2$ and 1.2 mL volume were examined for its power generation efficiency. The results of the study indicated that high energy upto $500\,W/m^3$ was generated because of the accessibility of large surface area for the oxygen reduction reaction [62]. The versatility of energy production was studied by employing flat plate MFCs with various organic substrates. A flat plate MFCs constituted of only a single electrode and membranous separator and exhibited minimum internal resistance by producing $\sim 286\,mW/m^2$ energy using acetate as substrate [63]. Large numbers of efforts are made to overcome disadvantages of dual-chambered MFCs related to separators.

## Single-chambered MFCs

Single-chambered MFCs have simple organization, which comprises both anode and cathode in the same chamber (Fig. 10.2). One of the studies suggested that decreasing the space in between the anode and cathode electrodes also reduces ohmic resistance. This problem can be solved busing catholyte that associates two electrodes in the chamber and increases the energy output. A single-chamber MFC having four pairs of electrodes generated trice the energy than the MFCs with a single pair of electrodes. In another experiment, three graphite brush-like anodes were assembled with a single cathode in single-chambered MFCs. It eliminated ~90% of chemical oxygen demand from wastewater and generated $975\,mW/m^2$ of energy. A hexagonal

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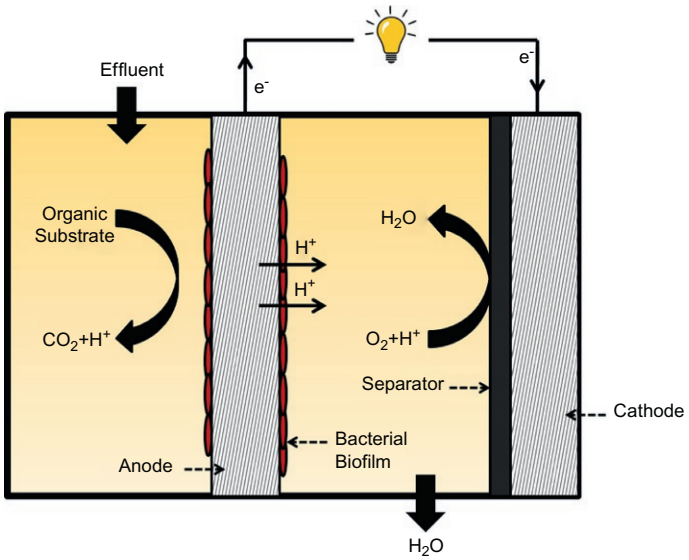


**FIG. 10.2**

Schematic representation of single-chambered MFCs.

MFC was introduced containing 11 pair electrodes that demonstrated high energy production potential (4.66 W/m$^3$) using distilled water as fuel [64]. Along with advantages like high-power generation, many disadvantages are associated with single-chambered MFCs. The problems like reverse transport of oxygen from cathode to anode and microbial adulteration are yet to be solved.

## Stacked MFCs

A stacked MFC is usually an arrangement of certain MFCs that are organized in serial or parallel arrangement to increase the energy yield as shown in Fig. 10.3. In general, a single unit of MFCs can produce the highest open-circuit voltage of 0.8 V [65]. Hence, if numerous MFCs are arranged parallely or serially, the resultant energy output is multiple of individual MFC unit energy outputs. Several operational parameters affect the final energy output of the stacked MFC. For instance, the ultimate voltage of the stacked MFCs was found to be lesser than the sum of individual MFC's voltages. This is probably due to the loss of energy during arrangement of MFCs in serial or parallel configuration. The stacked MFCs that are connected parallelly exhibited greater oxygen reduction reaction than serially arranged stacked MFCs. Additionally, elimination of chemical oxygen demand and high-power generation with minimum internal resistance was offered by parallelly stacked MFCs.

In one of the studies, six MFCs were stacked serially and parallely with copper wires. Acetate was used as an organic substrate in anodic compartment and ferricyanide was used as a catholyte in cathodic compartment. It was concluded that serially

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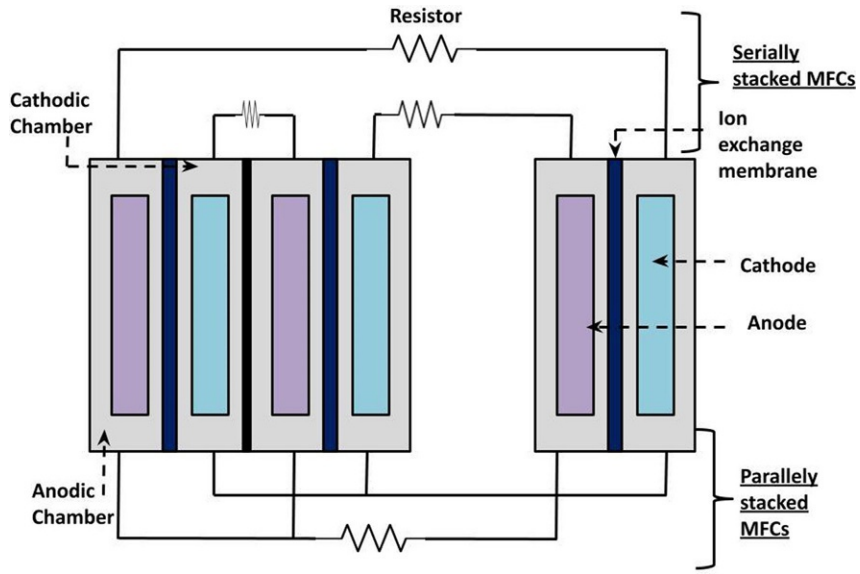


**FIG. 10.3**

Illustration of serially and parallelly stacked MFCs.

stacked MFCs generated 59 $W/m^3$, whereas parallel stacked MFCs produced 51 $W/m^3$ of energy [66]. However, in serially connected MFCs, the loss of the bio-activity of bacteria observed due to fuel starvation. Therefore, parallely connected MFCs arrangement is generally preferred over serially arranged stacked MFCs.

## Upflow MFCs

An upflow type of MFCs is cylindrical in shape and encompasses anode compartment at the base and cathode compartment at the top. The schematic representation of a model upflow MFC is shown in Fig. 10.4. These compartments are separated using glass rod/glass bead sheet. The organic substrates are provided from the base of an anode and progress toward the cathode. This generates electrical gradients in between the electrodes and ultimately generation power.

The power generation in this kind of MFCs is carried out in the absence of any catholytes or anolytes. Additionally, transfer-associated difficulties are very few due to the absence of any physical barriers [67]. Scale-up studies of upflow MFCs are comparatively easy. The major disadvantage of using this type of MFC is that the cost energy required for pumping the fuel in the system is much higher than the energy output [68]. Hence, it can be concluded that upflow MFCs can be used in the treatment of the wastewater and not for energy production [69]. An upflow MFC has major applications in research of energy production with minimal internal resistance and complex design of electrodes, glass separators, etc.

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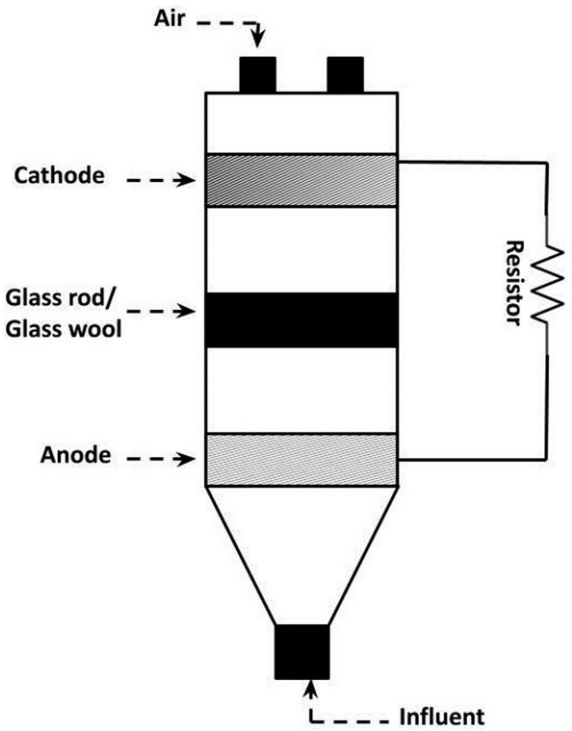


**FIG. 10.4**

Schematics of upflow MFCs.

## 3. Biological factors influencing the performance of MFCs

Two important biological factors that are responsible for change in the performance and output of MFCs are the (a) type of inoculum and (b) substrate used for oxidation in anode chamber. A detailed look into each of the factors is provided further.

### 3.1 Type of inoculum

The generation of bioelectricity from MFCs depends highly on the microorganisms that are used as inoculum. The charge transfer resistance that is developed at the bioanode is determined by the various methods by which the inoculum microbes carry out exocellular electron transfer [28,70]. The generation of anaerobic microbial biofilm is significant for degradation and generation of power in MFCs, which is why it is necessary to ascertain the method by which the organism carries out electron transfer along with the type of microorganism to be used as inoculum.

In the initial stages of research involving MFCs, nonelectrochemically active bacteria were used as inoculum coupled with synthetic mediators. The earliest

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and most path-breaking research in this field was presented by Kim et al. [71]. They reported that different *Shewanella putrefaciens* strains, viz., MR-1, IR-1, and SR-21 demonstrated electrochemical activity when grown anaerobically, but the same strains showed no such activity when cultivated aerobically. It was shown that these organisms had the ability to participate in the direct electron transfer outside the cell membrane to the anode.

Successive researchers mostly used electrochemically active bacteria (EAB), otherwise known as electricigens or current-producing bacteria, which possessed the unique ability to facilitate the transfer of electrons either directly or indirectly of electrons to the anode [72]. The respiration of the bacteria at the biocathode or bioanode is a result of the energy conservation with the electron transfer from EAB. The use of different cultures of microorganisms or types of inoculum affect the generation of current because the internal resistance of the anode depends on these factors. The inoculum in MFCs can be subdivided into two categories – pure and mixed cultures.

### 3.1.1 Pure cultures used as inoculum

The pure cultures used in MFCs are usually EAB, due to which they bring about the formation of a thin layer that is able to conduct electricity, during their respiration at the anode. This is the reason why pure cultures have been known to produce a superior power output as compared to mixed cultures. Additionally, the use of pure cultures was reported to reduce the start-up time for current generation considerably, as opposed to a longer start-up time experienced in case of mixed cultures [28]. A detailed classification of the various types of pure cultures used as inoculum in MFCs.

Archaea are capable of surviving in extreme conditions such as high pressures, temperatures, salinities, extremely high or low pH, which acts as potential stressors for the microorganisms, imparting upon them a unique electrochemical activity [73]. An MFC designed by Abrevaya et al. [74], used two Archaea species, viz., *Haloferax volcanii* and *Natrialba magadii*, as EAB inoculum in the MFC anode. They returned a peak current density of 49.67 and 22.03 $\mu A\,cm^{-2}$, respectively, and a power density of 11.87 and 4.57 $\mu W\,cm^{-2}$, respectively. The addition of neutral red as electron mediator improved the power density for both species and as compared to the power output of *Escherichia coli* under the same conditions, the power output was considerably higher [74].

Acidobacteria are acidophilic bacteria that show wide physiological diversity and inhabit various environments in nature. Their substrate utilization capacities are quite wide as well [73]. A number of Acidobacteria have been shown to be electrochemically active. Reduction at the electrodes was reported when *Geothrix fermentans,* an iron-reducer, was used as an electricigen in the MFC. The current generation reportedly reached up to 0.6 mA and electron recovery percentage was 97% [73,75]. *Arcobacter* sp. was also reported to account for about 90% of the bacterial load in an acetate-fed MFC and resulted in a peak power density of 296 $mW\,L^{-1}$ [73,76].

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Another class of pure cultures that have researched about considerably and used in MFC studies, are cyanobacteria. The MFCs that use cyanobacteria as electricigens are termed photosynthetic MFCs (PMFCs), wherein light works as the source of power and electricity is generated via light-catalyzed oxidation of water [73]. A peak power density of 6.5 mW $m^{-2}$ was reported on using *Spirulina platensis* as the inoculum [77]. The cyanobacteria *Synechocystis* PCC-6803 was used in a dual-chamber MFC, and the power density thus acquired was reported to be 72.3 mW $m^{-2}$ [78]. *Nostoc* sp. ATCC 27893 was used to generate power densities of 35 mW $m^{-2}$ and current density of 250 mA $m^{-2}$ [79]. Another study by Ciniciato et al. [80], witnessed the use of *Synechococcus elongates;* however, it did result in a promising amount of electricity generation.

Firmicutes, or bacteria with thick cell walls, show lower electrochemical activity due to their lower efficiency in transporting electrons from cell wall to electrode. However, some successful isolates like *Clostridium butyricum, C. beijerinckii*, *Methylomusa anaerophila*, and *Thermincola* sp. strain JR were shown to be used in MFCs for current generation [73,81–85].

Proteobacteria are the dominant class of microbial strains used in the inoculum for MFCs, as most of these bacteria are able to directly transfer electrons to electrodes. They are of four types, viz., α-, β-, γ-, and δ-proteobacteria.

α-Proteobacteria being mostly phototrophs are applied for use in PMFCs. *Rhodobacter sphaeroides* was declared to be the most efficient *Rhodobacter* species as the power output provided by the single-chamber PMFC using this organism went up to 790 mW $m^{-2}$ [86]. The first strain of bacteria used in PMFC was *Rhodospirillum rubrum*, and later was able to generate power density of 1.25 W $m^{-2}$ when used in a dual-chamber PMFC [87,88]. The use of *Rhodopseudomonas palustris* in MFC produced a power density as high as 2720 mW $m^{-2}$, and this was further improved after knockout of nitrogenase gene of the species, bringing the power density of the mutant strain from 11.7 μW $cm^{-2}$ to 18.3 μW $cm^{-2}$ [89,90]. *Ochrobactrum anthropi* and *Acidiphilium cryptum* were reported to produce 89 and 12.7 mW $m^{-2}$ power density, respectively [91,92].

The only β-proteobacteria that has been studied and reported as a successful inoculum for MFCs is *Rhodoferax ferrireducens*, which produced current density of 31 mA $m^{-2}$ in a glucose-fed dual chamber MFC [7].

γ-Proteobacteria have been the most extensively applied inoculum in MFCs. *E. coli* was shown to reach peak power densities up to 1304 mW $m^{-2}$ when used in a double-chamber MFC [93]. Another significant member of γ-proteobacteria that has been utilized for MFC inoculum as electricigens is *Shewanella*. *S. putrefaciens* was first used by Kim et al. in a lactate-fed MFC [94]. Afterward, Qiao et al. [95], developed a modification to *S. putrefaciens* by coating it with uniform nano-flaky nickel oxide so that it shows enhanced adhesion to the electrode. The MFC performance was enhanced and the new power density was 1024 mW $m^{-2}$. *Shewanella oneidensis* was also investigated for its use as electricigen in MFC. Its strains MR-1 and DSP10 were shown to be widely successful in enhancing performance of MFCs [96,97]. A genetically engineered strain of *Pseudomonas aeruginosa*

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was also shown to be successful as an electricigen in MFCs and a maximum current density of $0.5\,\mu A\,cm^{-2}$ was obtained [98]. A gene from *Geobacter sulfurreducens, pilT*, was used to induce hyperpiliation (increasing number of pili) in *P. aeruginosa* and its use in MFC demonstrated maximum current density of $35\,\mu A\,cm^{-2}$ [99].

The last class of proteobacteria, i.e., δ-proteobacteria, contains two genera, *Geobacter* and *Geopsychrobacter*, both of which contain many different species that have been applied as the inoculum in MFCs. *G. sulfurreducens* has brought about the highest current density among all the bacteria isolated for this purpose to date, due to its ability to retain its viability for a long time after attaching to the electrode [73]. The first investigation of this bacterium for use in MFC revealed a $1143\,mA\,m^{-2}$ current density [100]. Subsequent balancing of the anode using potentiostat brought about a current density of $2.26\,A\,m^{-2}$ [101]. Nevin et al. [102], obtained current density of $4.56\,A\,m^{-2}$ and power density of $1.88\,W\,m^{-2}$ using *G. sulfurreducens*. An MFC being used for the treatment of domestic wastewater that was inoculated with *Geobacter metallireducens* was reported to produce power density of $26\,mW\,m^{-2}$ and current density of $125\,mA\,m^{-2}$ [53]. Furthermore, *Geopsychrobacter electrodiphilus* isolated from marine sediment MFCs produced a current density of $6.6\,mA\,cm^{-2}$ in a malate-fed MFC [103].

Yeasts such as *Saccharomyces cerevisiae*, *Candida melibiosica*, and *Arxula adeninivorans* have also been used in MFCs [104–106] and produced power densities as summarized in Table 10.2. Eukaryotic algae like *Chlamydomonas reinhardtii* and *Chlorella pyrenoidosa* have been applied and produced favorable results as inoculum in MFCs [107,108].

However, the use of pure cultures also poses a number of challenges and drawbacks, such as high risk of contamination of the pure culture, and use of limited types of substrates. Moreover, for large-scale application of MFCs, it is preferred that mixed cultures like anaerobic digester sludge can be used because of their ready availability in large quantities and higher tolerance to environmental variations [28].

### 3.1.2 Exoelectrogens isolated from MFCs

The isolation of exoelectrogens from MFCs is very rare, but it is not unheard of. A wide range of microbes are found adherent to electrodes in MFC systems, in the form of biofilms. The discovery of biological laser printing for the isolation of pure EAB was made by Ringeisen et al. [109]. Another experiment by Zuo et al. [92] is involved in the isolation of *Bacteroides* sp. W7, a bacterium that reduces Fe(III) by fermentation, from the anolyte of a microbial electrolysis cell (MEC). The isolation of *Ochrobactrum anthropi* YZ-1 was carried out using dilution-to-extinction methods with the use of a U-tube MFC. Other exoelectrogens isolated from MFCs were *Aeromonas hydrophila* and *Clostridium butyricum* EG3 [84].

### 3.1.3 Mixed cultures used as inoculum

The use of mixed culture in MFC requires a longer time for start-up than that required when pure cultures are used. Thus, mixed cultures are also associated with a longer time to reach a stable power output [28]. Use of a diverse range of electricigens can

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**Table 10.2** Examples of different microorganisms used as pure culture inoculum for MFCs.

| Class of microorganism | Species used | Power density | Current density | Reference |
|---|---|---|---|---|
| Archaebacteria | *Haloferax volcanii* | 11.87 $\mu W cm^{-2}$ | 49.67 $\mu A cm^{-2}$ | [74] |
| | *Natrialba magadii* | 4.57 $\mu W cm^{-2}$ | 22.03 $\mu A cm^{-2}$ | |
| Acidobacteria | *Arcobacter* sp. | 296 $mW L^{-1}$ | NR | [76] |
| Cyanobacteria | *Spirulina platensis* | 6.5 $mW m^{-2}$ | NR | [77] |
| | *Synechocystis* PCC-6803 | 72.3 $mW m^{-2}$ | NR | [78] |
| | *Nostoc* sp. ATCC 27893 | 35 $mW m^{-2}$ | 250 $mA m^{-2}$ | [79] |
| **Firmicutes Proteobacteria** | | | | |
| α-Proteobacteria | *Rhodospirillum rubrum* | 1.25 $W m^{-2}$ | NR | [88] |
| | *Rhodopseudomonas palustris* | 2720 $mW m^{-2}$ | 0.99 $mA cm^{-2}$ | [90] |
| | *Ochrobactrum anthropi* | 89 $mW m^{-2}$ | 708 $mA m^{-2}$ | [92] |
| β-Proteobacteria | *Rhodoferax ferrireducens* | 12.9 $mW m^{-2}$ | 31 $mA m^{-2}$ | [7] |
| γ-Proteobacteria | *Escherichia coli* | 1304 $mW m^{-2}$ | NR | [93] |
| | *Shewanella putrefaciens* | 1024 $mW m^{-2}$ | NR | [94] |
| | *Shewanella oneidensis* | 249 $mW m^{-2}$ | 515 $mA m^{-2}$ | [97]; [96] |
| | *Pseudomonas aeruginosa* | NR | 35 $\mu A cm^{-2}$ | [99] |
| δ-Proteobacteria | *Geobacter sulfurreducens* | 1.88 $W m^{-2}$ | 4.56 $A m^{-2}$ | [102] |
| | *Geobacter metallireducens* | 26 $mW m^{-2}$ | 125 $mA m^{-2}$ | [53] |
| | *Geopsychrobacter electrodiphilus* | NR | 6.6 $mA cm^{-2}$ | [103] |
| Yeasts | *Saccharomyces cerevisiae* | 25.51 $mW m^{-2}$ | 282.83 $mA m^{-2}$ | [106] |
| | *Candida melibiosica* | 185 $mW m^{-3}$ | NR | **[105]** |
| | *Arxula adeninivorans* | 1.03 $W m^{-3}$ | NR | **[104]** |
| Eukaryotic algae | *Chlamydomonas reinhardtii* | 12.95 $mW m^{-2}$ | NR | [107] |
| | *Chlorella pyrenoidosa* | 6030 $mW m^{-2}$ | NR | [108] |

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contribute to more efficient generation of current and power [73]. Due to the strict operational conditions involved in the use of pure cultures, and the limitation of substrates that can be used in the same, miscellaneous or mixed cultures have emerged as a boon for the utilization of complex substrates.

Wastewater can directly be applied as the inoculum for MFCs. Wastewater from industries like distillery, sugar beet processing, breweries, chocolate industry, slaughterhouse industry and gum industry have been shown to achieve successful power densities [73,110–113].

Activated sludge can also be used as the inoculum for MFCs, first demonstrated by Dentel et al. [114] and obtained 517 mV voltage [114]. A single-chamber ethanol-fed MFC using activated sludge from wastewater treatment industry was reported to produce peak power density of 488 $mW\,m^{-2}$ [115]. The inoculation of fly ash leachate into various culture media produced activated sludge that resulted in a power density of 5.43 $W\,m^{-3}$ in the MFC [116].

It may pose a challenge using mixed cultures from wastewater and activated sludge because the communities are very complex and the method of current generation cannot be determined. To this end, scientists developed defined co-cultures, in which inoculum was produced by systematic selection of the microorganisms. The first such system was established by Qu et al., and contained *G. sulfurreducens* and *E. coli,* and it provided a better performance than that of the MFC inoculated with a pure culture of *G. sulfurreducens* [117]. Due to the excellent capacity of *Pseudomonas aeruginosa* to produce electron mediators, its cocultures are regarded as highly efficient. This property of *P. aeruginosa* was tapped while using its coculture with *Enterobacter aerogenes* as the biocatalyst in the MFC's anodic chamber and after optimizing the system for amount of dissolved oxygen, a 400% improvement in current production was observed [118]. Other cocultures like that of *P. aeruginosa* and *Klebsiella variicola* produced a maximum current density of three times higher than that produced by these two strains in isolation [119]. Cocultures of microorganisms were witnessed to widen the range of carbon sources for the microorganism in MFCs. Because no microorganism can concurrently participate in biomass degradation and electrons at the same time, cocultures proved to be a blessing in cellulosic biomass-fed MFCs [73]. One example of such a system was developed by Ren et al., which used a defined coculture of *Clostridium cellulolyticum* working as cellulose degrader, and *G. sulfurreducens* which acted as electricigen. This system returned promising results of power densities of 143 and 59.2 $mW\,m^{-2}$ from two different kinds of cellulosic substrates respectively [120].

Table 10.3 summarizes the different mixed cultures that have been used as inoculum in MFCs.

## 3.2 Substrate in anodic chamber

The substrate is a very significant factor that affects the performance of an MFC. A variety of substrates have been utilized in studies revolving around MFCs, from simple compounds like glucose and acetate, to complex compounds comprising algal

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**Table 10.3** Examples of different mixed cultures used as inoculum for MFCs.

| Type of mixed culture | Power density | Current density | Reference |
|---|---|---|---|
| **Wastewater** | | | |
| Diluted distillery wastewater | $168\,mW\,m^{-2}$ | $580\,mA\,m^{-2}$ | [112] |
| Sugarbeet processing wastewater | $14.9\,mW\,m^{-2}$ | $85\,mA\,m^{-2}$ | [113] |
| Brewery wastewater | $3022.39\,mW\,m^{-2}$ | $111.94\,mA\,m^{-2}$ | [111] |
| Slaughterhouse wastewater | $267\,mW\,m^{-2}$ | NR | [110] |
| **Activated sludge** | | | |
| Activated sludge from wastewater treatment industry | $488\,mW\,m^{-2}$ | NR | [115] |
| Activated sludge obtained by inoculation of fly ash leachate | $5.43\,W\,m^{-3}$ | NR | [116] |
| **Co-cultures** | | | |
| *Clostridium cellulolyticum* and *Geobacter sulfurreducens* | $143\,mW\,m^{-2}$ | NR | [120] |

NR, *not reported.*

and cellulosic biomass. The substrate affects the variation in the composition of the biofilms formed on the anode.

The theoretical potential of the anode (keeping a reference or standard hydrogen scale as a reference) can be calculated using the reference potentials of the components of the reaction, or the Gibbs-free energy of the reaction:

$$E^{\circ} = \frac{-\Delta G_r}{nF} \tag{10.3}$$

The theoretical potential at nonstandard conditions may be calculated on combining Eq. (10.3) with the Nernst Equation and the reaction quotient ($\Pi$)

$$E^{\circ} = \frac{-\Delta G_r}{nF} - \frac{RT}{nF} \ln(\Pi) \tag{10.4}$$

### 3.2.1 Type of substrate

MFCs are able to take into use a vast range of substrates in the anode chambers, from simple organic molecules to complex wastewater. The substrates act as the carbon and energy source for the bacteria used in the MFC. Some studies have also demonstrated the use of cysteine, human feces wastewater, and paper industry waste as substrates in the MFC anodic chamber [65,121–123]. Wastes released from breweries, dairies, and oil refineries, as well as wastewater from food processing units and domestic wastewater, have also been reported as suitable substrates for MFCs

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[124–127]. Recently, even urine has been reported to be an efficient feedstock for the MFCs [127–130]. Use of complex substrates generally helps to establish a microbial community that is diverse and active in the anodic chamber.

The efficiency of generation of energy starting from the substrate material depends on its concentration, composition, and characteristics. The substrate type affects the performance of the MFC by affecting the composition of the bacterial populations present in it and thus affects the current density of the bioanode [131].

Substrates can further be classified into simple or defined substrates and complex or undefined wastewater substrates. The former category includes:

**(i)** carbon source wastewater or substrates, such as hexose and pentose sugars, sugar derivatives, and polyalcohols,
**(ii)** nitrogen source wastewater or substrates, such as proteins and amino acids, and
**(iii)** organic acids and miscellaneous substrates, like acetic acid, butyric acid, alcohols, naphthalene, benzidine [132].

The latter category of complex and undefined substrates includes wastewater effluents from various industries, such as food and food processing industries, beverage industries, confectionary industries, dairy industries, agro-processing industries, livestock industries, refineries and distilleries, mining and related industries, pharmaceutical industries, paper and pulp industries, textile industries, petrochemical industries, and domestic and municipal wastewater. Pandey et al. have enlisted the variety of substrates previously recorded for use in MFCs [132].

The major substrate used for bioelectrochemical systems like MFCs is acetate, due to its simple nature and extensive use as a carbon source for stimulation of EAB. It is also an end product of a number of metabolic pathways for higher order carbon sources [126]. Liu et al. [133] utilized acetate for this purpose and achieved power density of $506\,mW\,m^{-2}$, which was 66% higher than the power generated ($305\,mW\,m^{-2}$) by using butyrate as the substrate [133]. A study by Chae et al. showed that among four different substrates (acetate, butyric acid, propionic acid, and glucose), acetate-fed MFC returned the most promising Coulombic efficiency (72.3%) [134]. Acetate has also been used as a substrate for MFCs that are inoculated with *G. sulfurreducens* [132].

Another very common substrate used in MFCs is glucose. Kim et al. were the first to report that glucose-fed cells in an MFC-containing *Proteus vulgaris* run for a shorter time as compared to galactose [135]. On using ferric cyanide as biocathode oxidant, Rabaey et al. reported that a glucose-fed MFC produced a maximum power density of $216\,W\,m^{-3}$ [136]. In 2008, Hu compared the power generation capacity of anaerobic sludge with that of glucose. While anaerobic sludge was able to generate very little power ($0.3\,mW\,m^{-2}$), glucose in the same MFC produced power up to $161\,mW\,m^{-2}$ [137]. Subsequent research by Chae et al. [134] revealed that among four different types of substrates, viz., acetate, butyrate, propionate, and glucose, resulted in the lowest Coulombic efficiency, however, this wide substrate specificity of glucose-fed MFC was explained by Chae et al., by proposing a more complex and miscellaneous consortium of electricigens to be present.

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Lignocellulosic biomass is another substrate that is widely used in MFCs. The abundance and renewability of these materials make them very feasible for use as feedstock for inexpensive energy production. Lignocellulosic biomass, however, is not feasible to be utilized as it is by the microbes present in the MFC. They must be degraded into monosaccharides or other compounds with a low molecular weight [126]. Use of cellulose as the substrate required the presence of both cellulolytic and electrochemically active bacteria, as discussed previously in the MFC designed by Ren et al. [120].

A popular complex substrate is wastewater from breweries. This is mainly due to the low strength of the wastewater obtained from breweries as well as its suitability for power generation in MFCs because it is derived from food and owing to its low concentration of toxic substances like ammonia that are usually present in animal wastewaters [126,138]. It is also ideal for use in MFCs owing to its high content of carbohydrates and low concentration of ammonium-associated nitrogen. Feng et al. [138] investigated the use of air-cathode MFC using beer brewery wastewater and obtained a promising power density of $528\,mW\,m^{-2}$. Wang et al. [139] also used beer brewery wastewaters to achieve power density of $483\,mW\,m^{-2}$ [139]. Wen et al. [140] also reported a maximum power density of $669\,mW\,m^{-2}$ when running an air-cathode MFC on raw continuous beer brewery wastewater [140].

One of the most popular MFC substrates obtained from the food processing industries is the starch processing wastewater (SPW), which consists of a high amount of carbohydrates that ranges from 2300 to 3500 mg/L, sugar content of around 0.65% to 1.18%, protein content of 0.12% to 0.15%, and starch contents ranging from 1500 to 2600 mg/L. This shows that SPW is an energy-rich resource that possesses the potential to be converted into a variety of useful products. Also, the biological conversion of SPW is useful in terms of recovery of resources like microbial bioprotein and biopesticides [126,132]. A maximum potential density of $239.4\,mW\,m^{-2}$ was obtained from an MFC designed by [141].

Table 10.4 lists the different substrates used in MFCs.

**Table 10.4** Examples of different substrates used in MFCs.

| Substrate | Power density | Reference |
|---|---|---|
| Acetate | $506\,mW\,m^{-2}$ | [133] |
| Glucose | $216\,W\,m^{-3}$ | [136] |
| | $161\,mW\,m^{-2}$ | [137] |
| Beer brewery wastewater | $528\,mW\,m^{-2}$ | [138] |
| | $483\,mW\,m^{-2}$ | [139] |
| | $669\,mW\,m^{-2}$ | [140] |
| Starch processing wastewater | $239.4\,mW\,m^{-2}$ | [141] |

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### 3.2.2 Concentration of substrate

The COD concentration of the influent substrate in MFCs greatly influences the amount of power generated in both fed-batch and continuous modes. Since the current generation in an MFC is proportional to the capacity of the microorganism to oxidize the substrate and engage in transfer of thus produced electrons to the anode, higher concentration of substrate results in larger amounts of generated power in a wide concentration range. The effect of substrate concentration on the performance of an MFC was studied by Martin et al. [142] in a continuous air-cathode glucose-fed MFC. The influent COD ranged from 200 to 8000 mg/L with a hydraulic retention time of 12 h. The increase in COD concentration up to 4 g/L led to an increase in power generation, but the power generation decreased upon increasing the COD levels up to 8 g/L. It was also observed that increase in substrate loading resulted in decrease in COD removal efficiency. Another study on this topic was conducted by Cheng and Logan [143], wherein an acetate-fed MFC was evaluated for its efficiency in power generation in varied conditions of influent COD concentration. They found that the increase in substrate concentration produced similar increases in maximum power density of the 28 mL MFCs. It was also found that at low substrate concentrations, the power generated can be affected negatively by the performance of the anode and not the cathode.

## 3.3 Methanogenesis in microbial fuel cells

Fermentable organic substrates lead to the fermentation of substrates by the action of fermenting bacteria in anodic communities. During this process, the substrates are rapidly metabolized and other microorganisms that carry out respiration at the anode are provided with easily biodegradable compounds. Fermentation might prove disadvantageous, as it leads to the liberation of hydrogen gas that supports the growth of hydrogenotrophic methanogenic bacteria, and these bacteria cause loss in Coulombic efficiency, which is one major limitation of organic carbon oxidation [28]. Periodic aeration of the anodic chamber to remove these methanogenic populations can be an efficient method of reducing the Coulombic losses.

As discussed above, MFCs used for the wastewater treatment are usually preferred to contain mixed consortia instead of pure cultures as inoculum, when the substrate is of complex type. The methanogens present in mixed cultures are responsible for methanogenesis, while EAB are responsible for the generation of bioelectricity [144]. Both of these species grow at the same conditions of operation. This synergistic action of methanogens and electricigens facilitates quicker reduction of BOD and COD [145,159]. A study by Sasaki et al. demonstrated methanogenesis in bioelectrochemical reactors that did not possess membranes between cathode and anode chambers for the first time. The inoculum used was seed sludge, while the substrate used was artificial garbage slurry consisting of dog food and water. The results of this study indicated that methanogenesis was almost identical in membrane and membrane-less bioreactors. Methanogens frequently participate in substrate competition with the exoelectrogens in MFCs [146].

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### 3.4 Start-up time for the operation of the MFC

The time taken for the MFC to obtain a stable and maximum power density, from the time of beginning its operation, can be termed as the start-up time of the MFC. It may range from a few hours to a few months. The maximum benefits of MFC used for wastewater treatment are reaped when the start-up time is low, as simultaneous harvest of energy can also occur. The long start-up time might be brought about by numerous factors including lack of electron donor, an electrolyte having a low ionic strength, long duration required for adaptation to the biofilm formed by the EAB, etc. The start-up time may be reduced by various strategies like reducing the magnitude of the applied external resistance, which helps to promote growth of biofilm, or providing carbon sources like glucose and acetate in wastewater with low BOD. Pretreatments carried out on the inoculum have also been reported to lessen the start-up time of the MFC. These include heating, chemical and enzymatic treatment, pH (acidic or alkaline) treatment, oxygen shock, shock loading, freezing, infrared radiation, etc. These treatments facilitate the electricigens to participate in substrate utilization, and as a result, result in electrogenic biofilm formation [28].

## 4. Chemical and operational factors influencing the performance of MFCs

### 4.1 Substrate type

As discussed in Section 3.2.1, the type of substrate considerably affects the performance of the MFC. A variety of substrates have been used in research involving electricity production and wastewater treatment using MFCs. Simple materials like glucose and acetate, which are easily degradable, are able to generate more power as compared to complex substrates such as real wastewaters from different industries. Due to its inert nature, acetate has been a favorite compound to be used as substrate. It is also the terminal product of a number of metabolic pathways for complicated organic substrates. Liu et al. [147] observed two times the amount of power output from acetate-fed MFCs as opposed to protein-rich wastewater-fed MFCs.

### 4.2 External resistance

External resistance (denoted by $R_{ext}$) is a big parameter in controlling the energy generation ability of an MFC. This factor is responsible for regulation of the availability of the anode for being an electron acceptor, as well as the electron flux throughout the circuit [28]. The external resistance applied to the MFC was shown to produce an effect on various aspects of the MFCs such as generation of current, removal of COD, and yield of biomass. A lower external resistance often leads to less yield of biomass from MFC than that of the conventional anaerobic digestion experiments used as control. In the laboratory, MFCs are mostly operated with a constant external resistance. In 2011, Jung and Regan evaluated the effects of $R_{ext}$ on acetate and

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glucose-fed MFCs. In the acetate-fed MFCs, they observed average current density to range between 40.5 mA $m^{-2}$ at 9800 Ω and 284.5 mA $m^{-2}$ at 150 Ω. In the glucose-fed MFCs, the current density ranged from 40 mA $m^{-2}$ at 9800 Ω to 273 mA $m^{-2}$ at 150 Ω. They also studied the morphology, active biomass components, extracellular polymeric substances (EPS) content and structure of the biofilms developed at different external resistances [148]. A higher $R_{ext}$ leads to lower current and higher voltage, while lower $R_{ext}$ values result in higher current and lower voltage because of the limitations imposed by electrode kinetics on the transfer of mass and charge. The amount of energy that the bacteria gain is proportional to the number of electrons that are transferred to the anode. Lower $R_{ext}$ facilitates higher energy gain by the bacteria, thus increasing current generation. Another study revealed that on increasing the $R_{ext}$ from 50 to 100 Ω, an initial dip in the current was followed by a rise and stabilization of current in 20 min. On the other hand, the rise of $R_{ext}$ from 500 to 1000 Ω required 2 h for the current to stabilize [149]. These experiments show that selection of an optimum external load is very necessary in order to harness the best output of power from the MFC.

## 4.3 Organic loading rate (OLR)

The rate of conversion of substrate and formation of biofilm in the anodic chamber of the MFC are largely governed by the organic loading rate (OLR). This in turn depends on the chemical parameters of the waste that is being used as substrate. The fermentation of organic-based waste can lead to the formation of acidic metabolites that affects the electrolyte in the anodic chamber. The potential difference and Coulombic efficiency in MFCs are in close relation with the OLR, and a fluctuation in the OLR can also lead to a fluctuation in the electron transfer efficiency [150]. In 2005, Kim et al. carried out research on the performance of a longitudinal tubular MFC under varying OLR from 0.04 to 0.42 g/L d. It was observed that the rise in OLR led to a rise in the power obtained from the MFC. At the OLR of 0.42 g/L d and an internal resistance ($R_{int}$) of 56 Ω, the power obtained was 1.35 mW, while at an OLR of 0.04 g/L d and $R_{int}$ of 1760 Ω, the power output was merely 0.02 mW [151]. Zhang et al. conducted another study in which it was determined that increasing OLR from 0.65 to 5.2 kg COD/$m^3$/d led to a reduction in CE from 14.4% to 1.2% in an MFC with treating leachate [152]. In another experiment, it was observed that upon changing the hydraulic retention time and leachate COD concentration, the COD removal and current generation capacity were considerably affected by a rise in the OLR. However, the performance of the MFC decreased upon reducing the hydraulic retention time [153,160].

## 4.4 pH

pH is another very significant factor that governs the performance of the MFC. It affects both anodic microbial activity and reactions at the cathode. The anolyte can get acidified due to proton accumulation, leading to electrolyte alkalization in

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the cathodic part of the MFC. Thus, a drop in pH leads to a drop in the energy generation capacity of the MFC, and the stimulation of the EAB to produce electricity is also reduced [150]. It simultaneously causes an increase in pH at the cathodic chamber that results in the inhibition of oxygen reduction reaction [154]. The use of pH buffers like phosphate or bicarbonate buffer has been put forth, but Chen et al. [155] opined that this method would merely increase the operating cost and create further burden for the removal of phosphorus [155]. Conversely, it was observed that higher pH at the anode resulted in the increased removal of COD and improvement in the MFC performance. The optimal pH also depends on the type of microorganism being used as inoculum in the MFC [150].

## 4.5 Temperature

A vital factor in determining the electricity generation from MFCs is the temperature of the anolyte. Microorganisms fall into four categories based on their optimum temperature for growth, viz., psychrophiles (10–15°C and <20°C), mesophiles (25–40°C and <45°C), thermophiles (50–85°C), and hyperthermophiles (80–113°C). Several studies of EAB are mesophiles. Microbial reactions are hindered at extremely low and high temperatures because of denaturation of metabolic and life-supporting enzymes, due to which MFCs cannot be operated properly with such conditions [154]. In a study carried out by Behera et al., to discern the influence of temperature on the performance of double-chambered MFC between 20°C and 55°C, it was found that the highest removal of COD (84%) was obtained at an optimum temperature of 40°C [156]. Tee et al. [157] also revealed in their study of the performance of an MFC-AHS with palm mill oil as the substrate that the ideal operating temperature was 35°C and the maximum current density and temperature were linearly related at a rate of increase of $0.1772\,mA\,m^{-2}\,°C^{-1}$ [157]. It was suggested by Song et al. that the temperature during start-up time of the MFC is of utmost importance as it was observed by them that the MFC operation faltered and led to failure of MFC stabilization if the temperature was altered during start-up time [158].

## 4.6 Ionic strength and conductivity

The increase in ionic strength or conductivity leads to a decrease in the internal resistance of the MFC, consequently improving the generation of power in the MFC [28]. Liu et al. [147] observed that rise in ionic strength from 100 to 400 mM (and thus solution conductivity from 10 to 40 mS/cm), by the addition of NaCl resulted in a rise in power output from 720 to $1330\,mW\,m^{-2}$ [147]. Mohan et al. [67] showed that an increase in the concentration of phosphate buffer solution from 50 to 200 mM (i.e., solution conductivity from 7.5 to 20 mS/cm) led to an enhancement in the generation of power, but on further increasing the conductivity above 40 mS/cm, the MFC performance was affected negatively due to an increased overpotential of the anode, leading to a lower voltage in the circuit. This showed that the activity of the EAB was restricted due to high saline conditions [67].

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## 5. Future prospects

Due to the significant rise in global energy demand, it is necessary to discover a substitute for fossil energy or nuclear energy with the same promising results. The finding of electrically active microbes able to generate energy has become a fascinating area of research with an aim to engineer MFCs. MFCs are a substantial technique for wastewater treatment and electricity generation. MFCs demonstrate its wide range of applications like power generation, waste elimination, bioremediation, and sensoring for chemicals. The simultaneous generation of energy from wastewater along with removal of pollutants demonstrates its eligibility in remote regions. Different designs and modes of operations are developed for continuous energy production and wastewater treatment on a large scale. However, numerous problems need to be addressed to upgrade the performance of the MFCs. Several existing advantages help researchers to continue studies in MFC to find appropriate solutions to global environmental problems.

## 6. Conclusions

In comparison with other renewable sources of energy like wind and solar energy, MFC produces low power due to the several disadvantages associated with operating conditions. The commercialization of MFCs as a source of energy is hindered by several disadvantages like low power output, high cost of the components used in MFCs, high internal resistance, and reversible ion and oxygen transfer across membranes. A single unit of MFC generates the highest voltage of 1.1 V. However, the practically obtained voltage is always low due to several energy losses allied with transfer of ions through the membrane, increase in the internal resistance of MFCs, etc. Though enhancement in total energy output is studied by scaling up the performance of MFC, the energy attained is not proportional to the volume of anode chamber. However, significant development is attained to decrease the expenses of electrodes and separators used in MFCs. Researches on the selection of electron acceptor with suitable anode substrate are very essential to attain the goal commercialization of this technique. Introduction of mathematical modeling can facilitate optimization of operational parameters related to MFC performance. A large number of disadvantages are yet to be solved to engineer an economically viable MFC.

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CHAPTER

# 11

# Development of bioelectrochemical systems integrated nanocomposite membranes for wastewater management

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## 1. Introduction

Water is the most essential component for all living beings. However, fresh water makes up to 2.5% of the total water resources in the world. Industrialization led to the increase in wastewater from various sectors such as industrial, domestic, sewage, and agriculture. This rapid development accounts to the contamination of various water bodies [1]. The conventional wastewater treatment technologies are cost-intensive and energy consuming, with no valuable materials being regenerated. Therefore, to overcome the water scarcity alternative methods of obtaining fresh water such as desalination of seawater or wastewater treatment are being adopted across the world [2]. In this scenario, bioelectrochemical systems (BESs) came into picture, which contributed to sustainable technology for concurrent electricity production and wastewater treatment along with production of fuels and high-value chemicals using microorganisms. This technology uses versatile approach of various fields of microbiology, electrochemistry, bioelectrochemistry, biotechnology, environmental science, materials science, etc. [3].

A typical BES consists of two chambers an anode and a cathode where electrochemical reactions take place to generate electrons that move via an external circuit and ions that migrate through a separator. In this way, the chemical energy present in the wastewater can be converted to electrical or gaseous energy by using microorganisms as biocatalysts. Typical electron donors in the anode are organic matter in wastewater and electron acceptors in the cathode include oxygen, nitrate, protons,



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and various metal oxides that can be reduced [4]. BESs use microorganisms to facilitate oxidation/reduction processes through the release/capture of electrons from an electrode. The energy stored in domestic wastewater is almost nine times the energy required for its treatment using conventional technologies. The proper treatment of domestic and industrial wastes can be a useful source of energy [5,6]. In addition to providing fundamental research relating to electron transfer mechanisms and biosensor applications, BESs are potentially of great significance for several industrially relevant fields such as synthesis of fine and bulk chemicals, energy conversion, and storage and remediation processes [7].

BESs are advantageous over conventional biological treatment technologies owing to their energy recovery in various forms (e.g., electricity, hydrogen, hydrogen peroxide, methane, and ethanol). These integrated BESs have been expanded to desalination applications and have exhibited improved energy recovery and wastewater treatment efficiencies compared to conventional BESs [8,9]. The advantages of the technology include (1) enabling direct recovery of electric energy and value-added products; (2) good effluent quality and low environmental footprint can be achieved because of effective combination of biological and electrochemical processes; and (3) it is inherently amenable to real-time monitoring and control, which benefits good operating stability [10]. The microorganisms can use a direct or a mediated way to exchange electrons with the electrodes. Direct electron transfer implies the physical contact between the electrode surface and the microorganisms. Nanowires are conductive nanofilaments of proteins, which enable long-range electron transfer between microorganisms and the electrode surface. Mediated electron transfer mechanism for exchange electrons with the electrode involves the use of redox mediators, which can be self-secreted by cells or added to the medium such as phenazines, flavins, and quinones [11,12].

In this direction, the present book chapter emphasizes the recent advances in BES that were developed provides the overview of (i) types of membranes polymer, ceramic, and bio-based all types of BESs and their applications, (ii) impregnation of nanomaterials such as metal, semiconductor, and melanin nanoparticles onto membranes; (iii) hybrid BESs integrated with membrane-based technologies microbial desalination cells (MDCs), osmotic microbial fuel cells (MFCs), microbial reverse-electro dialysis cells, and pressurized filtration-MFCs; (iv) energy consumption and recovery; and (v) current challenges and future perspectives.

## 2. Types of membranes

### 2.1 Polymer-based membranes

Polymeric membranes are employed in numerous applications due to their cost-effectiveness, excellent process ability, good reproducibility, and versatility. These polymers are generally classified natural or synthetic based as on their source of origin. There are two classes of membranes depending on membrane material natural

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polymers such as cellulose acetate, starch, chitosan, gelatine, and polyvinyl al*co*hol are some examples and synthetic or man-made membranes, such as polymethyl methacrylate (PMMA), polypropylene oxide (PPO), polyvinyl chloride (PVC), polyvinylidence fluoride (PVDF) and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), polyvinyl acetate (PVA), and polyvinyl pyrrolidone (PVP) are some examples [13].

Hyperbranched polymer (HBP) is a highly branched three-dimensional macromolecule with irregular topological structure and abundant terminal functional groups HBP is used for the preparation or modification of various types of separation membranes, and the abundant terminal functional groups of HBP can provide more reaction sites this ensures salt retention in membranes helps in wastewater treatment [14]. [15] studied two types of novel membrane polymer, isosorbide-based poly(arylene ether sulfone) and poly (arylene ether ketone). These membranes were used to develop ultrafiltration (UF) membranes by the phase inversion technique and found that it can potentially replace petroleum-derived polymers such as polyethersulfone (PES) in polymeric membranes for water treatment. Radha and Sreekanth [16] found that inserting the phosphoric acid active groups to the polymer matrix enhanced the thermal stability of the pure PVA. Anticó et al. [17] showed a new polymer inclusion membrane (PIM)-based probe containing Cyphos IL 104 has been evaluated in natural water for the first time to perform Zn accumulation measurements and to model metal accumulation (Zn) in biofilm it was prepared in laboratories.

## 2.2 Ceramic-based membranes

Ceramics is an inorganic, nonmetallic solid that is prepared from powdered materials and fabricated into products through the application of heat and displays characteristic properties like high hardness, strength, low electrical conductivity, and brittleness. The commonly used ceramic membranes include γ-alumina, zirconia, silica conventional catalyst that supports in water treatment and separation. These materials gained importance because of their high temperature resistance, and high toughness. Alumina-based composite membrane and titania-based composite membrane are widely used in however harsh operational conditions, smaller pore size, low surface area, and instability of phase structure lead to the use of composite membranes.

The composite-type ceramic membranes are looked into, covering the four types of ceramic/ceramic membranes, nanoparticle-incorporated ceramic membranes, ceramic-metal–organic frameworks (MOFs) membranes, and ceramic-polymer membranes. Typically, these are crystalline compounds formed from metallic and nonmetallic elements such as aluminum and oxygen (alumina-$Al_2O_3$), silicon and carbon (carborundum-SiC), and silicon and nitrogen (silicon nitride-$Si_3N_4$). Compared to monolithic membranes, composite membranes are noted with improved performance or added functionalities in water and wastewater treatment. Composite-type ceramic membranes are promising for water and wastewater treatment owing to their improved performance and enriched functionalities in the active

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layers. The fabricated composite membranes were very stable in aqueous solution over a long period. Ceramic membranes are asymmetric in microstructure with a denser active layer on top of a more porous and larger particle substrate. The active layer plays a key role in separation, the substrate provides mechanical support on the membrane, and the intermediate layers are included to tailor the overall pore size, level of porosity, and mechanical robustness. Two fundamental configurations include flat-sheet type and tubular type in water and wastewater treatment.

### 2.3 Bio-based membranes

Biopolymers are derived from various sources such as vegetable sources that includes cellulose-based (polymers, alginate, polyisoprene, and starch), bacterial fermentation products (chitin, chitosan, collagen, and sericin), animal (polylactic acid, polyhydroxyalcanoates, and polybutylene succinate), starch, alginate, poly (lactic acid), silk, and poly (butylene succinate). These bio-based renewable resources research came into picture due to these natural polymers that are the potential candidates able to substitute the conventional ones for membrane preparation.

Bio-based membranes suffer from limitations such as poor mechanical properties and their production and development is still in its infancy. Addition of natural plasticizer additives, polymer blends, and nanoparticles can overcome this drawback. Some companies have been successful in fabricating membranes from biobased materials. As an example Dupont has successfully commercialized a Sorona polymer made from propanediol obtained from corn) made of 37% renewably materials. Using a novel spinning process, Dupont has been able to produce nonwoven and microporous films for air and liquid filtration applications.

## 3. Impregnation of nanomaterials onto membranes

### 3.1 Metal nanomaterials impregnated membranes

Metallic NPs exhibit high surface area to volume ratio at the nanoscale size. The most commonly used metallic NPs include titanium (Ti), aluminum (Al), magnesium (Mg), silver (Ag), and iron (Fe) NPs [18]. Silver NPs are synthesized by in situ reduction of silver ions within casting solution during the phase inversion process. Silver NPs enter the membrane structure after being dissolved in the casting solution and this caused an increase in hydrophilicity and decrease in fouling [19]. Further, silver nanocomposite polysulfone (PSF) membranes were proven to be effective against two strains of bacteria, *Escherichia coli* and *Pseudomonas mendocina*, that were found in wastewater [20]. Inhibition of bacterial growth was observed even in Ag NPs nitrocellulose membrane filters [21,22]. Cellulose produced by bacteria *Gluconacetobacter xylinus* is markedly different from cellulose obtained from trees and cotton. Ag NPs are impregnated into the bacterial cellulose (BC) through chemical reduction by immersing BC into the silver nitrate solution for the impregnation of NPs to the membrane [23]. Au NPs impregnated on sugarcane membrane exhibited

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the effective bacteria removal and the obvious inhibition zones against *Staphylococcus aureus* and *E. coli* bacteria [24]. Improved fouling resistance and enhanced hydrophilicity were achieved by optimized polymer blend with gold NPs. The increase in the concentration of gold NPs even resulted in higher removal of phosphorous [25].

Alumina NPs showed an effect on the performance of polyvinylidene difluoride (PVDF) UF membrane infiltration of wastewater polluted with petroleum wastage. The presence of alumina NPs changes the phase inversion process and affects the structure and performance of the obtained nanocomposite membrane. Metallic NPs control the permeability of membrane by filling the space between the polymeric chains. One of the polymeric membranes incorporated with iron compounds is Nafion, sulfonated tetrafluoroethylene-based fluoropolymer-copolymer [18]. Iron NPs were surface treated with a silane agent (APTES) in order to reduce their agglomeration before incorporating in PES membranes [26]. [27] observed that there is an increase in hydrophilicity and antifouling properties of the nanocomposite membrane as well as an increase in the permeability, while the separation percentage of the membrane remained constant when NPs were added at a concentration range of 0–4 wt%. NPs of alumina are used for the removal of Cd (II) as a result sorption capacity increases with increase in pH value from 4 to pH value of 7.

## 3.2 Semiconductor nanoparticles impregnated membranes

The semiconductor NPs like oxides and sulfide have been used in combination with membranes. Higher stability of sulfides in contrast to other chalcogenide compounds and their wide bandgap makes them much suitable for various membranes application further the oxides are capable of generating high radicals, which improves the efficiency treatment system. The incorporation of inorganic additives like ZnS NPs in PES membrane improved their antifouling performance. Further, ZnS NPs embedded PES membrane by phase inversion method is used for humic acid (HA) filtration and the 2-mercaptoethanol capped ZnS NPs embedded PES nanocomposite membranes improved antifouling properties and dye separation performance of reactive red 195 from 91.3% to 96.1% and an enhanced flux from 121 to 163 $L\,m^{-2}\,h^{-1}$. In addition, blending polyvinylidene fluoride (PVDF) with the synthesized graphene oxide-zinc sulfide (GO-ZnS) nanocomposites membrane exhibited a minimal fouling ratio and a higher flux recovery rate (Du et al., 2020). Utilizing CuS/BC hybrid gel membranes as a photothermal conversion layer and their efficiency reached upto 98.5% [24]. CuO@CuS/PVDF membrane are synthesized by coprecipitation combined with microwave treatment, which is employed to activate persulfate (PS) toward degrading tetracycline (TC) leading to a greatly enhancement of removal efficiency 87.4% within 3 h.

$TiO_2$ NPs have proven to be successful in mitigating fouling of organic matter onto PES. Even their tensile strength and hydrophilic property were also enhanced after impregnation with $TiO_2$ NPs. $TiO_2$@GO NPs provided hydrophilic property in

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the membrane that improved membrane morphology and performances in term of permeate water flux and contaminants rejection [1]. As the concentration of $Al_2O_3$ NPs increased in the PVDF membrane, an improvement in the UF was observed [19]. The MgO mesoporous nanofibers studied the adsorption capacity against fluoride and congo red as the MgO NPs the mechanism of the adsorption process is based on electrostatic attraction and the surface complexation between the dye molecule they were found to carry out oxidative degradation by cleavage of the P—S bond or P—O bond of organophosphates and degradation of chlorpyrifos by destructive chemisorption [28]. Ceramic membranes modified by $Fe_3O_4$ NPs displayed superior antifouling resistance owing to the particles strong hydrophilicity and catalytic activity [13]. The Mg-based nanocomposites fabricated by electrospinning process are materials with ideal characteristics for being used in adsorption due to their large surface area.

## 3.3 Melanin nanoparticles impregnated membranes

Melanin is a prominent biopigment derived from the amino acid tyrosine in the living systems. Melanin displays extensive molecular recognition chemistry, with the ability to bind a wide range of organic and inorganic species. The metal ion chelating property of natural melanin is exploited for the removal of heavy metals from contaminated water. Melanin-based coatings derived by the extraction of melanin from human hair and the biomimetic tyrosinase catalyzed oxidation of L-dopa has shown to bind $Pb^{2+}$ ions with reasonable affinity and high capacity with the synthetic eumelanin coating binding up to 9% of its mass in lead [29]. Considered by mass bound, the synthetic eumelanin-coated discs have a much higher capacity for $Pb^{2+}$ than for $Cu^{2+}$, $Cd^{2+}$, or $Zn^{2+}$, however, on a per mole basis, the capacity for $Cu^{2+}$ is slightly higher than for $Pb^{2+}$. It was found that the affinity of the synthetic eumelanin coating for $Pb^{2+}$ is slightly higher than $Cu^{2+}$ and higher than for $Zn^{2+}$ and $Cd^{2+}$ [30]. According to [31], melanin that is extracellularly synthesized by the marine bacterium *Pseudomonas stutzeri* is used as the adsorbent. Melanin was coated on hydrophilic PVDF membrane matrix both in batch and continuous adsorption studies. Batch studies on the effect of pH, temperature, and adsorbate dose and continuous adsorption studies on the effect of flow rate, adsorbate, and adsorbent mass loadings were carried out by using biosynthesized melanin-coated PVDF membranes for the removal of Hg(II), Cr(VI), Pb(II), and Cu(II). Melanin-coated PVDF discs showed high potential to remove heavy metals from the aqueous phase even at very low concentrations (LCs) and have huge potential to be used in large-scale continuous mode operations. The maximum removal percentages of heavy metals achieved by melanin-coated PVDF membranes under batch mode operation were 87.6%, 88.45%, 91.8%, and 95.8% for mercury, chromium, lead, and copper, respectively, optimized at 318 K and pH of 3 for chromium and pH of 5 for other metals [31] (Table 11.1).

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**Table 11.1** Impregnation of nanomaterials onto membranes.

| Sl. no. | Name of Nanomaterial | Morphology and size of nanomaterial | Type of membrane | Parameter studied/focus | References |
|---|---|---|---|---|---|
| **Metal nanomaterial impregnated membranes** | | | | | |
| 1. | Nano-$TiO_2$ and graphene oxide (GO) | $6.27 \pm 0.44$ nm<br>Surface had visible pores and voids and nanoparticle nodules | Polysulfone (PSf) | Organic removal—60.98%<br>Ammonia removal—91.27% | [1] |
| 2. | Gold | 0.24 nm<br>Crystal structure with lattice fingers | Sugarcane | Catalytical efficiency for removing methylene blue—>98.3%. Effective bacteria removal and the obvious inhibition zones against *S. aureus* and *E. coli* bacteria | [24] |
| 3. | Magnetic $CuFe_2O_4$ | 3D coral-like layered multichannel structure | Eggshell membrane (ESM) | Adsorption capacity: Congo Red—199.23 mg/g, 4-nitrophenol degradation %—98.9%<br>Antibacterial properties against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) | [24] |
| 4. | Iron oxide | Less than 4 nm<br>negatively charged smooth hydrophilic surface | Ceramic | % Rejection<br>Natural organic matter—humic acid (HA) sodium salt—>90% | [13] |
| 5. | α-Zirconium phosphate | 130.7 nm<br>Porous with small pores on the surface | Polyvinylidene fluoride (PVDF) | Removal efficiency: $Cd^{2+}$—42.8%, $Cu^{2+}$—93.1%, $Ni^{2+}$—44.4%, $Pb^{2+}$—91.2% and $Zn^{2+}$—44.2% | [32] |

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**Table 11.1** Impregnation of nanomaterials onto membranes—cont'd

| Sl. no. | Name of Nanomaterial | Morphology and size of nanomaterial | Type of membrane | Parameter studied/focus | References |
|---|---|---|---|---|---|
| 6. | $Fe_3O_4$-$SiO_2$-$NH_2$ | 4.71 nm<br>Asymmetrical surface with a high density in the upper layer and a high porosity in the lower layer | Polyethersulfone (PES) nanofiltration | Removal efficiency<br>Cd(II)—93%<br>Methyl Red dye—97%<br>Enhanced salt rejection and antifouling property | [33] |
| 7. | Curcumin—Boehmite (B-Cur) | PES/B-$Cur_{0.5}$–<br>0.82 nm Globe-shaped morphology | Polyethersulfone (PES) nanofilteration | Adsorption capacity: $Pb^{2+}$ 35.01 mg/g, $Ni^{2+}$ 32.20 mg/g, $Cu^{2+}$ 31.12 mg/g, $Fe^{2+}$ 29.08 mg/g, $Zn^{2+}$ 27.08 mg/g and $Mn^{2+}$ 25.32 mg/g | [34] |
| 8. | Ferrihydrite | 10 nm<br>Asymmetric and porous structure with a finger-like macrovoids layer | Polyethersulfone (PES) | Adsorption capacity<br>$Pb^{2+}$ 64.77 mg/g | |
| 9. | 3aminopropyltriethoxysilane—$Fe_3O_4$ | 12.15(±0.1) nm<br>Heterogeneous surface with asymmetric structure composed of a skin-layer and porous bulk finger-like channels | Poly ethersulfone (PES) | Adsorption capacity Ar(V) 14.6 mg/g | [26] |
| **Semiconductor nanomaterials impregnated membrane** | | | | | |
| 10. | Cadmium sulfide (CdS) | ~5 nm<br>Particle-like morphology, which is interconnected meshwork made up of fibers | Eggshell | Catalytic degradation efficiency Mn(IV) ~93% | [35] |

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| | | | | | |
|---|---|---|---|---|---|
| 11. | Zinc oxide (ZnO) | 341.7 nm Thin and dense layer with finger-like micro-voids as supporting structure | Polyethersulfone (PES) | % Rejection<br>COD—82.6%<br>BOD—82.11%,<br>ammonia—57% | [1] |
| 12. | Titanium dioxide-doped hydroxyapatite ($TiO_2$-HAP) | 20–30 nm<br>Spherical and rod shaped | Polysulfone (PSf) | Degradation efficiency<br>chloramphenicol antibiotic—61.59% | [36] |
| 13. | Tungsten trioxide ($WO_3$) | 50 nm<br>Highly disordered porous morphology with homogeneous layer of small round nanoparticles | Bucky paper | Degradation kinetic constants<br>Methylene Blue—<br>$0.085 \pm 0.002\,min^{-1}$<br>Indigo Carmine<br>$-0.064 \pm 0.001\,min^{-1}$<br>Diclofenac sodium—<br>$-200.019 \pm 0.00\,min^{-1}$ | [37] |
| 14. | $CuFe_2O_4$ | 60 nm<br>Nano cubes | Polyvinylidene fluoride (PVDF) | Catalytic degradation efficiency<br>Congo red −95%<br>% Rejection<br>Congo red—99% | [38] |
| 15. | $CdS/Bi_2WO_6/ZnO$ | 17.23 nm<br>Mesopores on the nanoflakes | Polyvinylidene fluoride (PVDF) | Degradation efficiency<br>Nitrite ($NO_2^-$) ions—92.58% | [39] |
| **Melanin nanomaterials impregnated membrane** | | | | | |
| 16. | Dopamine-melanin | 80 nm<br>Uniform incorporation of nanospheres in membranes | Cellulose triacetate (CTA) nano filteration | % Rejection<br>$MgSO_4$ 97.6%<br>$Na_2SO_4$ 96.5%<br>$MgCl_2$ 91.8%<br>NaCl 76.1% | [40] |

*Continued*

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**Table 11.1** Impregnation of nanomaterials onto membranes—cont'd

| Sl. no. | Name of Nanomaterial | Morphology and size of nanomaterial | Type of membrane | Parameter studied/focus | References |
|---|---|---|---|---|---|
| 17. | Fungal melanin | 55 ± 8 nm Spider-web-like secondary structure nanofiber | Polyurethane (PUR) and polycaprolactone (PCL) | Removal efficiency PUR/melanin $Pb^{2+}$ 94.8 ± 4.0%, $Cd^{2+}$ 55.9 ± 2.5% $Ni^{2+}$ 40.9 ± 3.8%, $Cr^{3+}$ – 36.8 ± 3.5% PCL/melanin: $Pb^{2+}$ 97.7 ± 12.8%, $Cd^{2+}$ 45.5 ± 3.3%, $Ni^{2+}$ 39.8 ± 3.6%, and $Cr^{3+}$ 37.1 ± 5.8% | [41] |
| 18. | Melanin | Surface roughness of membrane increased with reduced pore size | Polyvinylidene fluoride (PVDF) | Removal efficiency Hg(II)—87.6% Cr(VI)—88.45% Pb(II)—91.8% Cu(II)—95.8% | [31] |

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# 4. Hybrid BESs integrated with membrane-based technologies

## 4.1 Microbial desalination cells

MDC is considered as an eco-friendly technology for water purification, Single desalination-chambered MDC offers simple desalination of water [42]. The application of MDC for wastewater treatment at the industrial level could be an attractive alternative to reduce the cost of existing systems [14]. Multistage microbial desalination cell (MMDC), air-cathode microbial desalination cell (ACMDC), bio-cathode microbial desalination cell (BCMDC), photosynthetic microbial desalination cell (PMDC), ozone-cathode microbial desalination cell (OCMDC), microbial capacitive desalination cell (MCDC), cuper-capacitive microbial desalination cell (SCMDC), upflow microbial desalination cell (UMDC), microbial electrodialysis desalination, and chemical production cell (MEDCC) are some of the MDC configurations [43]. Stacked MDC (sMDCs) consisting of multiple desalination chambers was introduced by Chen et al. [44] showed an improvement in charge transfer efficiency of MDC systems. Ziaedini et al. [45], examined two internally parallel and three internally series sMDC systems under continuous flow condition parallel configuration showed that decrease of intermembrane distance leads to lower salt removal efficiencies series configurations showed that at low NaCl concentrations, desalination efficiency decreases with an increase in the inter-membrane distance.

MDC is integrated with MFC technology and electrodialysis (ED) process to desalinate the saline water [46]. It consists of three chambers separated by an anion exchange membrane (AEM) next to the anode chamber, a cation exchange membrane (CEM) next to the cathode chamber, and the center chamber containing saline solution between the two membranes [47,48]. This system is based on the MFC structure, and its function is also the same. However, in addition to cathode and anode chambers, there is an intermediary chamber between cathode and anode that contains salt water, which is separated from anode by an AEM and cathode by a CEM [49]. In the anode chamber, bacteria degrade and oxidized the organic matter as a result of this oxidation process the electrons release and flow toward the cathode through an external electrical circuit [47]. MDC's performance is influenced significantly by reactor configuration, operational conditions such as the substrate, conductivity, charge transfer efficiency, electrode materials, resistance, hydraulic retention time (HRT), pH imbalance, and membrane [50].

MDC is a sustainable green desalination technology, a cost-effective approach for simultaneous wastewater treatment and recovery of value-added products (i.e., HCl, NaOH, $H_2O_2$, $H_2$, humic, and fulvic acid), and an electrochemical process for the removal of targeted pollutants (i.e., $NH_4^+$-N, Cu, Cr, Pb, Ni, and As). The enhanced performance was mainly due to the reduced internal resistance. Relying on the ability of the waterweed (*C. demersum*) to increase the concentration of oxygen in water, a plant microbial desalination cell (PMDC) was built and its performances were assessed based on its electricity productions, desalination, and

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wastewater treatment efficiencies, also found that there was a reduction in the COD value due to fermentation and or methanogenesis. Quadripartite microbial desalination cell (QMDC) was designed and fabricated by [51] to demonstrate the feasibility of a 9 chamber MDC for cotreatment of septage (septic tank sludge) and municipal wastewater. It was found that fouling, time progress, number of cells, and initial COD concentration can significantly affect QMDC performance. Salman and Ismail [47] studied the performance of a triple chambers MDC for the simultaneous desalination of wetland saline water, domestic wastewater treatment, and power generation, and 100% removal of COD from real wastewater was obtained from the anode chamber and also a maximum removal of TDS. Multichambered MDC was used to bioremediate steel plant wastewater using the same wastewater as a fuel for anodic bacteria. A pure culture of *Pseudomonas putida* was isolated and inoculated to remove toxic phenol [46]. [52] compared the performance of MDC using a single culture of *Debaryomyces hansenii* with desalination using *Saccharomyces cereviseae* and found that *D. hansenii* proved to have better performance. Nitrogen removal and recovery can be achieved by MDC systems.

## 4.2 Osmotic microbial fuel cells

Forward osmosis (FO) is an outlier because it relies on osmotic pressure rather than on an applied pressure, this is ideally in the range of pressures used in reverse osmosis (RO) for desalination, since FO membranes are also dense. Osmotic MFCs (OsMFCs) are a new type of MFCs with integrating. Both an OsMFC and an MFC achieved similar organic removal efficiency, but the OsMFC generated higher current than the MFC with or without water flux, resulting from the lower resistance of FO membrane. Recently, in attempts to support and improve the wastewater treatment capability of MFCs, an FO process, i.e., a membrane separation technology driven by the osmotic pressure difference between low (feed) and high (draw) concentration solutions across a semipermeable membrane has been retrofitted into a MFC, which is referred to as an OsMFC. OsMFCs, which have a semipermeable membrane as a separator between anode and cathode chambers, have subsequently achieved water recovery from wastewater in the anode chamber by using osmotic pressure as the FO process and concurrently accomplished electricity production from organic matter in wastewater by using electrochemically active bacteria. An OsMFC inherits the advantages of both MFCs and FO systems, generating electricity from the organics by exoelectrogens and extracting clean water from wastewater by FO membrane. This represents new synergy between BESs and FO and can be extended to microbial electrolysis cells (MECs) and MDCs for various purposes. Coupling the MFC (or MDC, MEC) with FO could achieve wastewater treatment, energy recovery and resource recovery (such as clean water, nutrients) in one system. The performance of the OsMFC was examined with either NaCl solution or artificial seawater as a catholyte (draw solution). A conventional MFC with a CEM was also operated in parallel for comparison. It was found that the OsMFC produced more electricity than the MFC in both batch operation (NaCl solution) and continuous

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operation (seawater), likely due to better proton transport with water flux through the FO membrane. Wastewater flows through the anode chamber where water is drawn across a membrane into the cathode chamber resulting in the generation of electricity an effluent prepared for aerobic digestion and saline water. The saline water can be further processed using desalination methods like RO to yield potable water. Owing to the addition of FO membrane, OsMFC has higher quality of the effluent water, lower investment, and larger bioelectricity generation compared with conventional MFCs for municipal wastewater treatment. Further modifications of MDCs enhance its applications such as a tubular/stacked configuration can be used for continuous operations, extraction of hydrogen gas from the cathode chamber by the additional supply of electric potential. Increased organic removal and desalination can be achieved by hydraulic linking of OsMFC with MDC. Membranes are operated by achieving a hydrostatic pressure greater than the osmotic pressure so as to drive water transfer through the membrane against the natural direction of osmosis, while the salts are retained and concentrated on the influent surface of the membrane. In OsMFCs, proton transport has no role in current carrying in the pH range of the electrolytes used.

Silver nanoparticle (AgNP) modified thin film composite (TFC) polyamide FO membrane showed advanced hydrophilicity, more negative zeta potential, and better antibacterial property. The biofouling mitigation of the FO membrane further improved the water flux and the electricity generation of the OsMFC. The model predicated the variation of internal resistance with increasing water flux and confirmed the importance of membrane resistance. Increasing water flux with higher catholyte conductivity could decrease the membrane resistance. The OsMFC incorporating silver nanoparticle-polydopamine-coated FO membrane exhibited less flux decline (22%) than the OsMFC with a pristine membrane (50%) due to an antibacterial ability of silver nanoparticle. MFC power density from 3 $W/m^3$ up to 11.5 $W/m^3$ organic (>95%) and phosphorus removal (>99%) and therefore maintained effluent COD below 20 mg/L. The OsMFC achieved water flux of 1.06–1.49 LMH and reduced wastewater effluent by 24.3%–72.2% depending on HRT. Increasing the recirculation rate of the catholyte from 100 to 3000 mL/min slightly improved water flux to 2.15 LMH. The low water flux was likely due to inefficient reactor configuration, membrane fouling, and concentration polarization. The OsMFC constantly produced bioelectricity and achieved a maximum power density of 28.2 $W/m^3$ from an acetate solution or 4.5 $W/m^3$ from domestic wastewater. OsMFC with another MDC that uses IEMs would increase the salt removal capacity to over 90% [53].

## 4.3 Microbial reverse-electro dialysis cells

Reverse electrodialysis (RED) is an innovative method to convert salinity gradient into useful power, based on the use of many pairs of anion and CEMs situated between two electrodes For the first time a microbial RED cell (MRC) was used for the treatment of water contaminated by Cr(VI). It has been recently shown that

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both inorganic and organic pollutants can be removed by RED processes using water with different salinity without the supply of electric energy. However, a high number of membrane pairs is usually necessary for the treatment of wastewater by RED. A microbial reverse-electrodialysis electrolysis cell (MREC) was used to produce hydrogen gas from fermentation wastewater without the need for additional electrical energy. Increasing the number of cell pairs in the RED stack from 5 to 10 doubled the maximum current produced from 60 to 120 $A/m^3$ using acetate. However, more rapid COD removal required a decrease in the anolyte HRT from 24 to 12 h to stabilize anode potentials. Hydrogen production using a fermentation wastewater reached $0.9 \pm 0.1$ L $H_2$/Lreactor/d, with $58 \pm 5\%$ COD removal and a coulombic efficiency of $74 \pm 5\%$. These results demonstrated that consistent rates of hydrogen gas production could be achieved using an MREC if effluent anolyte COD concentrations are sufficient to produce stable anode potentials. There are various technologies such as RED and pressure retarded osmosis (PRO) that produce electricity from salinity gradient. The RED stack consists of alternately stacked AEM and CEM separated by high concentration (HC) and LC cell. When HC and LC solutions are supplied into the RED stack, due to the concentration gradient, the cations in the HC solution migrate through the CEM and the anions migrate through the AEM to the LC solution. Results confirmed that assembling 11 cell pairs in RED stack of MERCC could meet the potential requirement of Bi film cathode for driving $CO_2$ reduction. The cell pairs, flow rate of the salt solution and the external resistance showed obvious effects on the MRECC performance. Under the optimal condition, the maximum formate concentration of $185.4 \pm 6.1$ mg/L and faradaic efficiency of $88.9 \pm 3.2\%$ were yielded with anodic COD removal up to $87.0 \pm 4.3\%$. Energy efficiency indicated nearly 5.8% of extracted energy from salinity gradient and wastewater had been utilized for $CO_2$ to formate conversion. Overall, MRECC exhibited a promising platform for $CO_2$ reduction and value-added chemicals production by using sustainable energy from wastewater.

## 4.4 Pressurized filtration-microbial fuel cells

Pressure-driven membrane filtration refers to the use of a transmembrane pressure difference as the driving force for permeation through a membrane. In accordance with the type of filtration membrane installed and the reactor configuration, PF-MFCs have been referred to as a bioelectrochemical membrane reactor, electrochemical membrane bioreactor, MFC-membrane bioreactor (MBR), UF-MFC, membrane bioelectrochemical reactor, and anaerobic membrane electrochemical bioreactor. However, all PF-MFCs share the same basic principles. Note that the basic design of a PF-MFC is almost identical to that of a conventional MFC, except for the filtration membrane. While energy recovery from organic waste is performed by coupling the bio-anodic oxidation and cathodic reduction reactions, purification of wastewater fed to the anode compartment is conducted by passing wastewater treated by EAB through porous membranes, such as DMs, MF membranes, and UF membranes. For wastewater purification, a low-level hydraulic pressure is required. Using these principles, PF-MFCs can remove COD, nitrogen, volatile

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suspended solids, bacteria, and viruses and consequently produce a better-quality final effluent than traditional MFCs. Although OMBRs are likely to have lower fouling propensity compared to the conventional pressure-driven MBRs with MF or UF membranes, fouling is still a major challenge where the concentrations of foulants are high. Most existing OMBR and/or OsMFC studies were performed with cellulose triacetate (CTA) based FO membranes.

The movement of feed water constituents through membrane is influenced by pressure gradient force, constituent's concentration in feed water, electrical potential of the membrane, feed water flow rate, temperature, and chemical properties of the feed water (like pH, dissolved organic carbon, nature of constituents, etc.) and the membrane. There also may be other factors that influence the filtration process. Depending on the pore size, pressure-driven membrane filtration process is generally classified into microfiltration (MF) (membrane pore size 0.1–10 μm), UF (membrane pore size 0.01–0.1 μm nanofiltration (NF) (membrane pore size 0.001–0.01 μm), and RO (membrane pore size ~0.0001 μm) (Table 11.2).

**Table 11.2** Hybrid BESs integrated with membrane-based technologies.

| Sl. no. | Cell design | Anode chamber | Cathode chamber | Removal efficiency | References |
|---|---|---|---|---|---|
| **Microbial desalination cell (MDC)** | | | | | |
| 1. | Cylindrical triple chamber | Plain graphite plate | Plain graphite plate | Chemical oxygen demand (COD)—80.2 ± 0.5% | [54] |
| 2. | Cylindrical four chambers | Graphite brush | Activated carbon air-cathode | Total chemical oxygen demand (TCOD)—57.2% | [24] |
| 3. | Triple chamber | Graphite rods | Circular stainless steel grid | NaCl salt—31% | [55] |
| 4. | Tubular two chamber | Carbon fiber brushes | Air-cathode | Chemical oxygen demand (COD)—85% | [42] |
| 5. | Stack cubic chamber | Carbon felt | Stainless steel mesh | Chemical oxygen demand (COD)—75.5 ± 1.4% Nitrogen—66 ± 5.3% Phosphate—66.7 ± 4.7% | [56] |
| **Osmotic microbial fuel cell (OsMFC)** | | | | | |
| 6. | Two chamber | Carbon cloth | Carbon cloth | Cr(VI)—97.6% | [57] |

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**Table 11.2** Hybrid BESs integrated with membrane-based technologies—cont'd

| Sl. no. | Cell design | Anode chamber | Cathode chamber | Removal efficiency | References |
|---|---|---|---|---|---|
| 7. | Two chamber | Carbon brush | Carbon cloth coated with Pt | Total organic content (TOC)—>99.0%<br>Total phosphorous (TP)—~95%<br>Total nitrogen (TN—$NH_4^+$—N)—~58.0% | |
| 8. | Two chambers | Carbon brush | Carbon cloth coasted with Pt | Total organic content (TOC)—96.6%<br>$NH_4^+$—N—78.7%<br>Total nitrogen (TN)—73.6%<br>Total phosphorous (TP)—30.6% | [58] |
| **Combined osmotic microbial fuel cell (OSMFC) and microbial desalination cell (MDC)** | | | | | |
| 9. | Rectangular two chamber OsMFC Upflow three-chamber MDC | Carbon fiber brush with a titanium wire | Carbon cloth | Chemical oxygen demand (COD)—93%<br>NaCl salt—48% | [59] |
| **Microbial reverse-electrodialysis cell (MRC)** | | | | | |
| 10. | Staked | Bio-anode | Abiotic—cathode | Chemical oxygen demand (COD)—87.0 ± 4.3% | |
| 11. | Staked | Graphite fiber brush | Wet-proofed carbon cloth | Chemical oxygen demand (COD)—52 ± 2.3% | [60] |
| 12. | Staked | Graphite fiber brush twisted by two titanium wires | Bi/Cu | Chemical oxygen demand (COD)—82% | [61] |
| 13. | Staked | Carbon fiber brush | Graphite plate | Total organic content (TOC)—99.6% | [62] |
| 14. | Staked | Carbon felt | Carbon felt | Cr(VI)—~100% | [63] |

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**Table 11.2** Hybrid BESs integrated with membrane-based technologies—cont'd

| Sl. no. | Cell design | Anode chamber | Cathode chamber | Removal efficiency | References |
|---|---|---|---|---|---|
| **Integrated ultrafiltration—Bioelectrochemical system (UF-BES) or microbial fuel cell and membrane bioreactor (PF-MFC OR MFC-MBR)** | | | | | |
| 15. | MFC-MBR anodic chamber/ cathode into an aerobic MBR PVDF membrane | Carbon fiber brushes | Carbon fiber brushes | Chemical oxygen demand (COD)—95.1% $NH_4^+$—N—95.2% | [64] |
| 16. | Two-compartment with polyethersulfone (PES) membrane for ultrafiltration | Carbon brushes | Carbon brushes | Chemical oxygen demand (COD)—80% | [65] |
| 17. | Tubular/two chambers Microfiltration membrane | Carbon brush | Brush bio-cathodes | Chemical oxygen demand (COD)—98.3 ± 0.3%, ammonia nitrogen—99.6 ± 0.1% Total nitrogen (TN)—80.0 ± 0.9% | [66] |
| 18. | Anoxic/oxic membrane reactor and an air–cathode MFC | Graphitic plates | Graphitic rod | Chemical oxygen demand (COD)—53.71% | [67] |

## 5. Energy consumption and recovery

Integrating membrane onto BES introduces new elements for energy recovery in the form of bioelectricity, along with further advancement toward the production of biogases like hydrogen, methane [68], and biofuels like ethanol and butanol [69]. Production of bioelectricity is done through the biodegradation of chemical energy stored in wastewaters by electroactive microorganisms [70]. The generated electricity could significantly reduce the economic burden to treat wastewater. An extensive amount of effort has been devoted to improving energy production in BES in different forms [71].

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Hydrogen ($H_2$) is a renewable fuel with various advantages of simple production from organic substrates and no pollutant emissions after combustion. A wide range of anoidic substrates including pure substrates (glucose, acetic acid, butyric acid, and alcohols), complex substrates (cellulose, starch, and sludge), and wastewater (industrial and domestic wastewaters) has been successfully employed for $H_2$ production with low energy inputs. Great efforts in optimizing the parameters like reactor configuration, electrode material, membrane, substrate, catholyte (electrolyte which is on the cathode side of an electrochemical cell), biofilm enrichment, applied voltage, pH, temperature, and other operational conditions were done to improve the $H_2$ yields [72]. A combination of microbial electro-synthesis (MES) with dark fermentation greatly enhanced the removal of organic matter and the yield of $H_2$ production. Hence, this combination is a promising perspective for simultaneous energy recovery and wastewater treatment.

Methane ($CH_4$) is another widely used energy source, as well as one of the target products in BES. Optimizing parameters like reactor design [73], pH, cathode material, and applied voltage [74] have led to elevated $CH_4$ production, which is helpful in expanding the BES applications. Alcohols are recently used as biofuels, a renewable energy source. They are produced by bio-electro synthesizing in BES. Compounds like acetic acid, glucose, glycerol, cellulose, wood residues, wastewater, and carbon dioxide were used to convert into ethanol, butanol, and propanediol for energy cogeneration [75,85].

Besides the recovery of different energy sources from wastewater through integrated BES, they simultaneously require energy for operating. Energy consumption contributes highly to operating costs. A study on OsMFC is showing that energy consumed by the system was about 0.81 $kWh/m^3$ in which 97.4% was due to catholyte aeration were as the rest was contributed by electrolyte/FO recirculation. Thus, the net energy value of the system and their energy consumption must be accessed accurately.

Analysis of energy balance on several hybrid BES found that apart from microbial reverse electro-dialysis cells (MREC), other systems including conventional microbial desalination cell (CMDC), OsMFC, and MBR had high energy requirements [9]. Even though there was low requirement of energy input, the energy retrieved was considerably low compared to an industrial scale. Certain suggestions to enhance the efficiency of the system targeting a zero net energy balance are as follows: (1) High input flow rate of saline water into desalination chamber and (2) improving desalination rate through enhanced applied voltage. It was found in a study that by the application of an external voltage of 1.1 V in an MDC, there was an increment in current generation from 670 mA to nearly 2000 mA along with the increase in salt removal rate from 3.7 to 9.2 $kg\,m^{-3}\,day^{-1}$ [53], (3) use of stored renewable energy for system operation, optimization of energy requirement for pumping, and (4) concentrating on self-energy sufficiency by optimizing the stack arrangement. It was reported that altering the arrangement of stack in a microbial reverse electro-dialysis cell (MREC) by placing an extra LC chamber adjacent to anode chamber has reduced ammonia crossover along with decreased ammonia

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nitrogen losses into anolyte (electrolyte which is on the anode side of an electrochemical cell) by 60%. It also increased the Coulombic efficiency to 83% and improved the $H_2$ yield to a maximum of 3.5 mol $H_2$/mol acetate, with an overall energy efficiency of 27% [76]. Further research on pursuing net-zero or positive energy systems promotes the reduction of capital cost along with efficient energy recovery, thus encouraging integrated BES as a promising technology for the treatment of wastewater.

## 6. Current challenges and future perspectives

The synergetic application of BES integrated with membrane technology has emerged as a promising yet challenging technology especially in the wastewater management and energy/resource recovery. Despite the rapid advancement, further research is necessary to overcome the current constraints related to the optimization of the system performance. In order to exploit the complete potential of the integrated system, it is important to overcome the inherent hindrances. Hence, in this section, the key challenges addressed to the further development of these systems are discussed. They are classified as follows: (1) technological challenges, (2) microbiological challenges, and (3) economic challenges [77,86].

Technological challenges deal with the difficulties in technical development of the system, and they are further divided into membrane-related issues, electrode potential losses, ohmic losses, and lastly the low treatment efficiency. Implementation of membrane-based water treatment technology incorporated with BES has made it more versatile and was capable of solving some existing problems of BES by laying advantages in its application by reducing the permeability of protons, loss of substrates, and back diffusion of oxygen [78,79]. These advantages are hampered by some core membrane-related challenges that led to problematic deployment and maintenance of membrane that presents technical barriers to the design, efficiency, and scaling up, hence need to be resolved. Some notable obstacles to membrane utilization include biofouling, internal resistance, and pH gradient [80]. Most of the membrane-related water treatment technology has faced the critical issue of membrane fouling resulting in the increase in capital cost and performance deterioration. It is also reported that fouling led to decrement in energy recovery. A study showed coating of polydopamine or anthraquinone/polypyrrole on membrane benefited in mitigating biofouling. Some factors affecting membrane fouling include membrane properties, sludge characteristics, and operational settings. Therefore, a better understanding of these influencing factors would help in further development of membranes by diminishing the problem of fouling. BES utilizes ion exchange membranes to maintain electro neutrality that enable the transport of ions across the membrane while keeping the anode and cathode reactions separated. Since the anode reactions are proton producing and the cathode reactions are proton consuming, this will cause a pH decrease in the anode chamber and a pH increase in the cathode chamber that can cause a significant decrease in the performance.

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An alternate method was suggested in avoiding the pH gradient by operating the system in a loop configuration such that there is an active transport of ions back to the respective chambers.

Internal resistance is an intrinsic property of BES that consists of ohmic, charge transfer and mass transfer resistance that increases the required voltage thus inhibiting the system performance. Moreover, it cannot be removed completely but can be reduced depending on the membrane types. Reduction of internal resistance was found in replacement of CEM—MEC (cation exchange membrane—microbial electrolysis cells) to FO—MEC (forward osmosis—microbial electrolysis cells). Emerging application of nanocomposite adsorptive membrane incorporated with nanosorbents in recent studies showed promising results through high adsorption, innate separation capacity, superior reusability, more permeation flux, enhanced catalytic performance, high microbial removal, and outstanding antifouling properties [13,24,35]. Then again, their practical applications have been limited by the aggregation of nano adsorbents in the membrane matrix. More researches must be encouraged to resolve this issue related to the modified membrane thus to improve and promote the overall performance of the integrated system. Furthermore, studies show that the use of hybrid BES managed to mitigate the pH imbalance through a self-generated pH control mechanism, reduce internal resistance, and enhance the recovery of bioenergy [42]. Potential losses or over potentials at the electrodes can significantly limit the attainable current densities, and therefore it is vital to minimize electrode potential losses to achieve high current densities. The electrode materials employed are required to exhibit high conductivity, mass transfer, large surface area, porosity, mechanical strength, scalability, biocompatibility, and chemical stability [81]. Commonly, graphite, platinum black, and platinum are utilized, but they are currently expensive, which not only limits scaling up but also pose technical and economic practicality, hence needed to be replaced with alternative catalysts such as stainless steel, nickel (Ni) [82], titanium (Ti) [82], nano-$Ni(OH)_2$, molybdenum disulfide ($MoS_2$), Si-coated $Fe_3O_4$ nanoparticles, copper-loaded carbon nanotubes (CNTs), plasma-treated Cu foil, and $Sn/SnO_x$ [83].

The opposition that ions and electrons experience when they are moving through an electrochemical system is referred as ohmic resistance. Higher the ohmic resistance and current density, the higher will be the resulting ohmic loss in a system. Since many real wastewaters have low conductivity, there is a considerable electrolyte ohmic loss. Very thin desalination stacks were operated to minimize ohmic resistance of desalination stacks, which resulted in attaining higher desalination efficiencies and power densities in MDCs. Low treatment efficiency was observed in direct comparison of the performances of the BES-MTs with actual wastewater/seawater leading to a very different performance. Reduction of desalination performance and water flux was displayed [84]. Hence, more studies must be conducted by employing actual wastewater. Microbiological challenges deal with the difficulties in complete utilization of microorganism in optimizing the system. Real wastewater is a source for a wide range of organic matter that makes it more complex. BES technology needs to utilize high diversity of microbial communities that is required to

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breakdown these organic matter. Decreased performance resulted by reduction in electron recovery was observed mainly due to inability of anodic microbial community to degrade complex material and competition in consuming substrates by methanogens. Some commonly used bacterial in BESs that uses glucose are *E. coli*, *Bacillus subtilis*, and *Proteus vulgaris*. *E. coli*, *P. vulgaris,* and *Pseudomonas methanica* use sucrose and acetate. Selection of mixed culture bacteria hinders the power output of the system. Lack of comprehensive knowledge of microbes makes it difficult in the choice of suitable culture that determines the performance of the system, hence needed to be solved.

## 7. Conclusion

In conclusion, several economic challenges are involved in the scaling up of integrated membrane-based BES with the most feasible strategies for realizing practical applications. Commercialization of integrated system must consider various factors such as reactor configuration, electrode and membrane materials, installation site, application purpose, electrical connectivity of the material applied, organic carbon sources, and electrolytes. Although the system can recover energy from wastewater, they simultaneously require energy to be operated, hence their energy consumption must be weighed as well. Even though the utilization of multiple unit system enhanced the performance of wastewater and desalination by undertaking these limitations, the scale and performances are not sufficient for the system to be deployed on a commercial scale.

Future research must be undertaken on integrated nanocomposite membrane BES to enhance the system's industrial competitiveness through increased power and current, reduced internal resistance, increased efficiencies, and reduced capital cost by discovering cheaper materials, and thus facilitating progress toward commercialization, eventually supporting the energy-sustainable alternatives and feasible wastewater treatment facility. However, further research is also needed to evaluate the long-term performance of continuous systems and their tolerance to changing environments. Although many drawbacks need to be overcome to realize the commercial applications of these systems, the rising demand for better technologies may create a revolution for the development of BES integrated nanocomposite systems. Thus, the future of integrated BES still remains encouraging.

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CHAPTER

# 12 Industrial wastewater treatment using bioelectrochemical systems and the potential for energy recovery

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## 1. Introduction

Despite the Earth being largely covered in water, fresh water for drinking, agriculture, and industrial purposes is a scarce resource. Of the world's water resources, only 3% is fresh water, the majority of which is stored in the form of ice in glaciers and not accessible for human consumption [1]. Furthermore, human activity, including industrial and agricultural use, generates large amounts of polluted water, which, when released untreated, pollutes even those limited fresh water resources, including surface and ground water reserves [2]. Polluted water contains many hazardous compounds, including polyaromatic hydrocarbons (PAHs), pharmaceuticals, heavy metals, etc., which can potentially cause serious health issues in humans [3]. For example, PAHs can cause cancer, kidney and liver disease, lung damage, damage to the central nervous system, birth defects, developmental disorders, and neurological issues [4]. Similar health effects on humans have also been reported due to heavy metal exposure. Moreover, due to nonbiodegradability and the persistent nature of heavy metals, they tend to bioaccumulate and became part of the ecosystems, which can have a long-lasting effect on the environment and also on living beings [5]. Hence, it is vital to treat polluted waters in order to protect the waterbodies and to prevent further environmental degradation.

The wastewater treatment systems include physical (screening, adsorption, filtration, oil skimming, etc.), chemical (precipitation, oxidation, coagulation, flocculation, neutralization, etc.), and biological (bacteria, fungi, archaea, aerobic, and



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anaerobic) methods [6,7]. The physical and chemical methods are highly effective for treating wastewater, but there are many drawbacks of these methods that make their application somewhat problematic. The physical treatment methods are cost intensive due to the high installation cost and sometimes due to the high replacement cost for certain parts such as membrane modules for filtration processes [8]. Again, in chemical methods, the requirement of chemical reagents involves cost and, due to their toxic nature, may cause secondary pollution. On the contrary, the biological methods are considered to be low cost, sustainable, and environmental friendly process for mitigating environmental pollution. In biological methods, pollutants are converted to less toxic forms with the help of microorganisms, and often, resource recovery in the form of energy or valuable products can be performed [9].

The most common biological wastewater treatments are the activated sludge process (aerobic) and anaerobic digestion (anaerobic); and both have their advantages, such as ease of operation, simple methods, low cost, and bioenergy production as biogas in the case of anaerobic digestion. Disadvantages include sensitivity of processes to environmental factors such as pH, temperature, pollutant concentrations, and difficulty to degrade nonbiodegradable pollutants, etc. [10,11]. However, in recent times, bioelectrochemical systems (BESs) have gained a lot of interest in terms of research, innovation, and publication. The significant increase in publications on wastewater treatment using microbial fuel cells (MFCs) in the last decade is depicted in Fig. 12.1. From the figure, it is also evident that this is not only at lab-scale, but also a large number of studies have been carried out on pilot-scale systems, indicating the maturity of this technology and its application potential at a commercial scale.

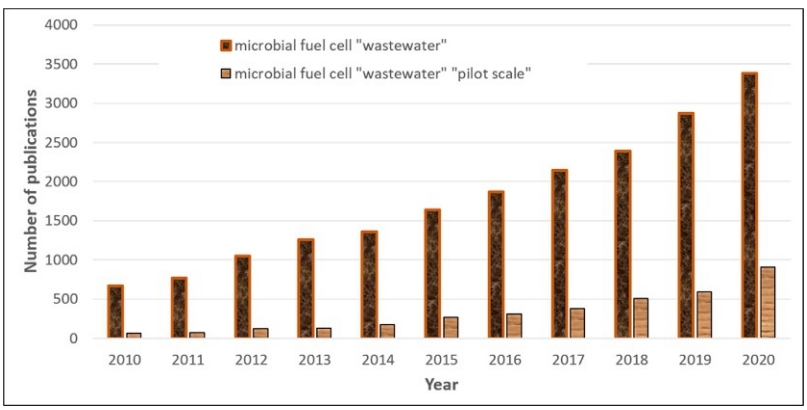


**FIG. 12.1**

Number of publications during the last decade on microbial fuel cells for wastewater treatment and on pilot-scale studies.

*Source: Google Scholar; legends indicate the keywords used.*

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BESs such as MFCs have the ability to convert chemical energy to electrical energy by degrading the organic compounds present in wastewater with the help of microorganisms [12]. This helps in simultaneous energy recovery from waste and wastewater remediation in a sustainable way. The energy recovery from wastewater using MFCs is a direct process, where electrical energy is produced [13], in contrast to other biochemical processes, such as anaerobic digestion or fermentation, where products such as methane, hydrogen, ethanol, butanol, etc., need to be further processed to remove impurities and then require subsequent application of conversion technologies to produce utilizable forms of energy [11]. MFCs have been utilized for treating wastewaters from domestic, agricultural, and various industrial sources such as dairy, petrochemical refining, animal farming, paper and pulp, brewery and distillery, pharmaceutical, food processing, edible oil processing, etc. Studies have reported remarkable results both for treatment efficiency and for energy generation (Tables 12.1–12.9). This chapter intends to provide detailed information on different wastewater treatment methods using MFCs.

## 2. Configuration and operational mechanism of microbial electrochemical systems

The microbial electrochemical systems concept is based on the ability of electrochemically active microorganisms to transmit electrons from a reduced electron donor to an electrode, and then to an oxidized electron acceptor, resulting in power generation [12,53]. The microbial metabolism of an organic substrate involves an oxidation reduction reaction, which in a combined way generates energy. Completing the electron transport chain requires an electron source (substrate) that is part of the microbes' metabolic flux and an electron acceptor (sink). The system consists of an ion-permeable membrane to separate the oxidation reduction reaction. Based on their usage, microbial electrochemical systems can be classified in four distinct configurations: (i) MFC, (ii) microbial electrolysis cell (MEC), (iii) microbial desalination cell (MDC), and (iv) microbial electrosynthesis system (MES) [54,55].

MFC is the most common form of bioelectrochemical cell, and consists of anode and cathode chambers separated by an ion-exchange membrane. The anodic chamber is biotic and contains microbes capable of degrading organic compounds (oxidation reaction) and generating electrons, which travel through the external circuit [54]. The cathode chamber is an abiotic compartment, where protons and oxygen react to form water (reduction reaction).

MEC is used for production of hydrogen utilizing organic matter; even the organic matter present in wastewater can be used in this case. The microbes present in the anode chamber degrade organic compounds to produce electrons, protons, and carbon dioxide, among which the free protons and electrons combine in the cathode chamber to produce $H_2$. However, this process requires an external supply of energy (greater than 0.2 V) to carry out the reactions [55,56].

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**Table 12.1** List of different domestic wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation (mW/m$^2$) | Reference |
|---|---|---|---|---|---|
| Domestic wastewater | Air cathode | 300 | 71 | 103 | [14] |
| Domestic wastewater | Upflow membraneless + photobioreactor | 238.7 | 77.9 | 481 | [15] |
| Domestic wastewater | Air-cathode | 345 | 54 | 22.5 | [16] |
| Human urine | Single compartment | 17,000 | 75 | NA | [17] |
| Human feces | Two chambered | 650 | 71 | 70.8 | [18] |

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**Table 12.2** List of different brewery and distillery wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation (mW/$m^2$) | Reference |
|---|---|---|---|---|---|
| Brewery wastewater | Air cathode | 2240 | 87 | 483 | [19] |
| Brewery wastewater | One chamber air cathode | 625 | 43 | 264 | [20] |
| Brewery wastewater | One chamber air cathode | 1501 | 47.6 | 669 | [21] |
| Brewery wastewater | Tubular air cathode | 2125 | 93 | 96 | [22] |
| Brewery wastewater | Serpentine type stack | 2120 | 86.4 | 97.2 | [23] |
| Brewery wastewater | Stackable baffled MFC | 800 | 87.6 | 181 | [24] |
| Distillery wastewater (molasses based) | Single chamber open air cathode | 15,200 | 72.8 | 124.35 | [25] |

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**Table 12.3** List of different agricultural wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Types of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Beet sugar wastewater | Upflow anaerobic sludge blanket reactor MFC | NA | 53.2 | 1410.2 | [26] |
| Beet sugar wastewater | Anaerobic baffled stacking microbial fuel cell (ABSMFC) | NA | 50–70 | 115.5 | [27] |
| Starch processing wastewater | Air-cathode MFC | 4852 | 98 | 239.4 | [28] |
| Molasses wastewater | Single chambered cuboid | 27,500 | 53.2 | 1410 | [29] |
| Rice milling effluent | Earthen pot | 2250 | 96.5 | 2300 | [30] |

**Table 12.4** List of different animal farming wastewaters utilized as substrate in MFCs and their corresponding performances.

| Animal farming wastewater type | Types of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Swine wastewater | Single chambered | 8320 | NA | 182 | [31] |
| Swine wastewater | Large scale single chambered | NA | 85.6 | 382 | [32] |
| Manure wash water | Air cathode single chamber | NA | NA | 215 | [33] |
| Cattle manure slurry | Air cathode cassette electrode | NA | 56.7 | 765 | [34] |
| Slaughterhouse wastewater | Dual chambered | 4850 | 93 | 578 | [35] |
| Animal carcass wastewater | Upflow tubular air cathode | 11,180 | 50.7 | 2190 | [36] |

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**Table 12.5** List of different landfill leachate wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Acidogenic food waste leachate | Dual chambered | 5000 | 90 | 15,140 | [37] |
| Acidogenic food waste leachate | Dual chambered | 1000 | 98.7 | 432 | [38] |

**Table 12.6** List of different palm mill oil effluents utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Palm mill oil effluent | Dual chambered | 1680 | 32 | 765 | [39] |
| Palm mill oil effluent | Cylindrical | 8000–10,500 | 90 | 765 | [40] |
| Palm mill oil effluent | Dual chambered | 38,400 | 54 | 765 | [41] |

**Table 12.7** List of different paper-pulp industry wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Paper recycling wastewater | Single chamber | 480 | 60 | 506 | [42] |
| Cellulose wastewater | Single chamber | 1500 | 50 | 1070 | [43] |
| Cellulose wastewater | Two chamber | 1500 | 70 | 880 | [43] |

MDC is a modification of the MFC system, where salt removal from saline wastewater and organics removal can be achieved simultaneously [57]. It can be differentiated from MFC by nonrequirement of an external bacterial mediator and reliance on internal electrically active microbial communities. The desalination chamber is generally located in between the anodic and cathode chambers, separated by an ion-exchange membrane.

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**Table 12.8** List of different petroleum wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Petroleum refinery wastewater | Dual chambered GC-packing type | 250 | 64 | 330.4 | [44] |
| Real-field petroleum sludge | Single chambered open air cathode | 3000 | NA | 53.11 | [45] |
| Total petroleum hydrocarbons | Sediment MFC | 18,590 | 24 | 2162 | [46] |
| Purified terephthalic acid wastewater | Single chambered | 8000 | 74 | 31.8 | [47] |

**Table 12.9** List of different pharmaceutical industry wastewaters utilized as substrate in MFCs and their corresponding performances.

| Wastewater | Type of MFC | Substrate concentration (mg COD/L) | COD removal (%) | Electricity generation ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Recalcitrant pharmaceutical industrial effluent | Single chambered air cathode | 79,800 | 68.5 | 205.61 | Velvizhi and Venkata Mohan [48] |
| Synthetic penicillin wastewater | Air cathode single chamber | NA | 87.1 | 10,1200 | Wen et al. [49,50] |
| Paracetamol-containing effluent | Dual chamber | 390 | NA | NA | Zhang et al. [51] |
| Steroidal drug production wastewater | Single chamber | 6720 | 82 | 22,300 | Liu et al. [52] |

Microbial electrosynthesis (MES) system is used for production of chemicals (such as acetate) from carbon dioxide by application of electrical energy. In this system, the water-splitting reaction results in production of electrons, protons, and oxygen in the anodic chamber [58]. Similar to the MECs, the protons and electrons combine in the cathode chamber to produce $H_2$, which, along

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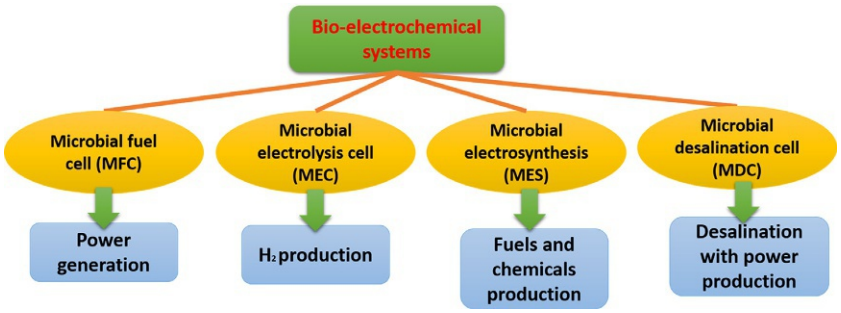


**FIG. 12.2**

Different bioelectrochemical systems and their applications.

with $CO_2$ supplied externally, is used by microbes to produce volatile fatty acids.

Among these different configurations, MFCs have been explored in most detail for wastewater treatment, including application in pilot study-scale setups [12]. Hence, in the following section, wastewater treatment using MFCs is discussed (Fig. 12.2).

## 3. Wastewater treatment using bioelectrochemical systems

MFCs have been widely reported in the literature for their capability to treat different wastewaters and generate power. The wastewater can vary in composition depending on its source (Fig. 12.3). The typical characteristics of industrial wastewater include

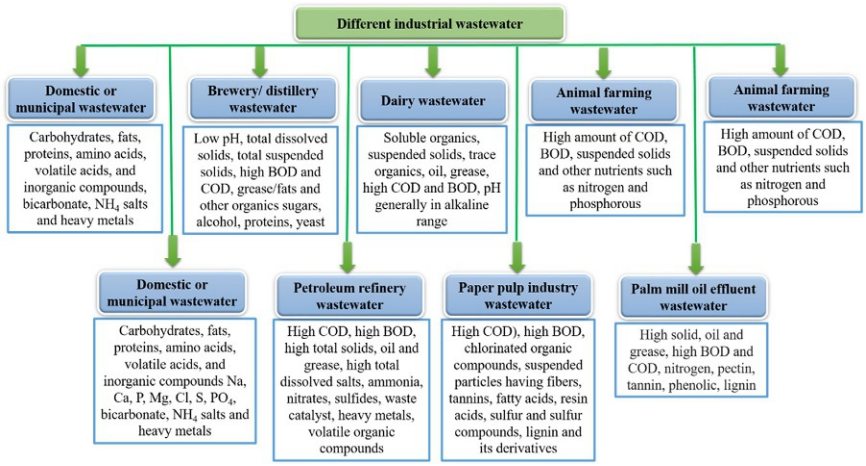


**FIG. 12.3**

General characteristics of wastewaters used in microbial fuel cells.

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chemical oxygen demand (COD), biological oxygen demand (BOD), nitrogen, phosphorous, sulfur, solids content, and alkaline pH. Apart from these main constituents, inorganics such as sodium, potassium, calcium, magnesium, iron, and heavy metals such as lead, cadmium, zinc, copper, nickel, cobalt, etc. are present in different concentrations. MFCs have been reported to remove most of these wastewater components successfully and generate treated water suitable for release to the environment [53].

Fig. 12.4 depicts the general mechanism of wastewater treatment using MFCs and the end products of various water pollutants. The carbon-containing organics are generally converted to $CO_2$ and water in the anodic chamber in MFC. Nitrogen compounds are biologically converted to ammonia and struvite ($NH_4MgPO_46H_2O$) through nitrification denitrification reactions. In MFC, the end product for phosphorous-containing compounds is struvite, which can be recovered and has some commercial value [13]. Heavy metals are nonbiodegradable, and hence, with the help of dissimilatory metal reduction in MFCs, they are precipitated and can possibly be recovered [55]. Sulfur compounds present in wastewater, such as sulfide, is oxidized in MFC to produce less toxic stable products, viz., elemental sulfur. In the following section, details of different industrial wastewater treatment using MFCs are discussed along with power generation in those studies.

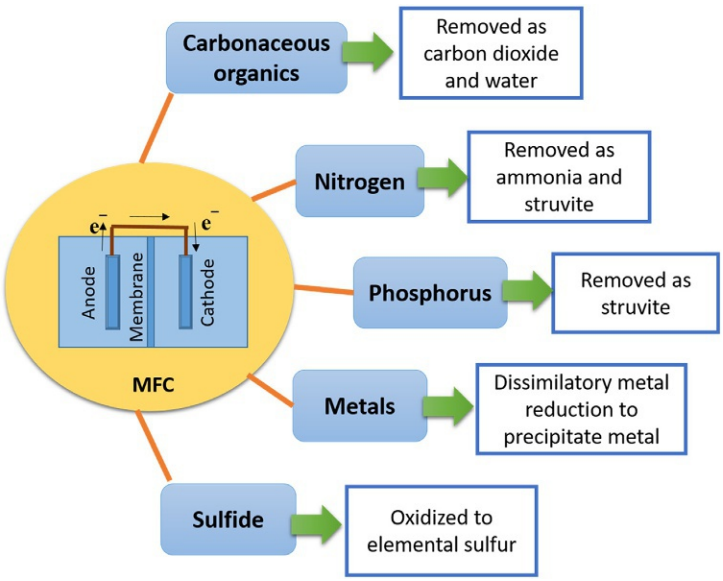


**FIG. 12.4**

Removal mechanism of various commonly available wastewater pollutants using microbial fuel cells.

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## 3.1 Domestic or municipal wastewater treatment

Domestic/municipal wastewater is generally considered a suitable substrate for MFCs because of the presence of various pollutants with less toxicity. In addition, ammonium recovery and power generation from urine separated from such wastewater is another advantage. In one such example, raw urine was used as a cheap substrate in single compartment MFC to remove impurities, electricity production, and nutrient recovery [17]. Fangzhou et al. [18] demonstrated that power could be generated from separated human feces (blackwater) using MFCs. Table 12.1 shows the treatment of different domestic and municipal wastewater using MFCs and its power generation efficiency and COD removal.

To treat domestic wastewater, a coupled system consisting of an upflow membraneless MFC (upflow ML-MFC) and a photobioreactor was developed [15]. The results showed 77.9% COD removal, 23.5% total phosphorus (TP) and 97.6% $NH4^+$-N removals, respectively, and 481 $mW/m^2$ electricity generation using upflow ML-MFC. However, the removal efficiency was increased to 99.3% TP and 99.0% $NH4^+$-N, when combined with a photobioreactor. You et al. [14] treated domestic wastewater using air cathode MFC and achieved COD removal of 71% and the value of electricity generation was 103 $mW/m^3$. Other researchers also used air cathode type MFC and achieved good results for electricity generation [16]. Human urine is a water contaminant that needs treatment, and can be used as a cheaply available substrate in MFCs for power generation. A high COD removal of 75% was obtained using single compartment MFC [17]. Fangzhou et al. [18] used human feces as substrate in two chambered MFC and results showed 71% of COD removal and 70.8 $mW/m^3$ electricity generation.

## 3.2 Brewery/distillery wastewater treatment

Brewery and distillery wastewater is also a suitable substrate for MFCs due to high organic content and a substantial lack of inhibitory substances. Different industrial operations, such as saccharification, fermentation, cooling, washing, etc., generate large amounts of brewery wastewater, with typical COD values of 3000–5000 mg/L (about tenfold that of domestic wastewater), the characterization of which shows the presence of sugar, starch, and protein components [59]. Conventional methods used to treat such wastewater include: aerobic sequencing batch reactors, crossflow ultrafiltration (UF) membrane anaerobic reactors, and upflow anaerobic sludge blanket (UASB). These methods are effective but require high energy and high operating temperatures (35–45°C) to achieve high treatment efficiency. On the other hand, better treatment along with energy generation is possible using MFC systems (Table 12.2). Dong et al. [24] demonstrated a full-scale (90 L), five modules, stacked system fed with brewery wastewater that achieved 88% COD removal and power generation of 171 $mW/m^2$. Feng et al. [19] used air cathode MFC to treat brewery wastewater and achieved very high power generation of 528 $mW/m^2$. In another study, brewery wastewater continuously treated using air cathode MFCs obtained 669 $mW/m^2$ [21].

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## 3.3 Agricultural wastewater treatment

The starch producing industry utilizes large amounts of water during its processing and hence, generates huge amounts of wastewater, which is characterized by high COD values of 16,870–22,800 mg/L. Such wastewater is also characterized by its high content of carbohydrates (2300–3500 mg/L), sugars (0.65%–1.18%), proteins (0.12%–0.15%) and starch (1500–2600 mg/L), making it an energy-packed resource that could impose a heavy load on the environment if not treated properly [60]. Due to this high organic content, such wastewater can also be converted into a wide variety of final products. Wastewater from cassava mills is also rich in content, such as COD, BOD, TSS, and low ammonium concentrations [61].

Molasses is widely used as a raw material in the fermentation industry due to its low cost and easy availability. It generates a high amount of wastewater, which needs to be treated before discharge into the environment. Different conventional, chemical, and biological methods have been used to treat such wastewater, but they have some limitations such as high cost and longer treatment time requirement. MFCs are one of the best alternatives to treat such wastewater and generate electricity but, due to the complex nature of this substrate, it is very difficult to obtain the desired high treatment efficiency and energy recovery [25,29,62,72].

Rice straw is also one of the cheap, easily available agricultural wastes, and is a suitable substrate for MFC. It is characterized by high amounts of cellulose, hemicellulose, and lignin. Behera et al. [30] used rice milling industry wastewater as substrate using earthen-pot MFCs and obtained a very high COD removal of 96.5%, power generation of 2.3 $W/m^2$, with additional 84% lignin and 81% phenol removal. Table 12.3 shows the different agricultural wastewaters utilized as substrate in MFCs and their corresponding electricity production performances.

## 3.4 Animal farming wastewater treatment

Animal farming wastewater includes wastewater generated from manure production and slaughterhouses. Such wastewater is mainly composed of biodegradable organic carbon, fats, and proteins [33]. There are several studies that have reported the use of manure and slaughterhouse wastewater as MFCs substrate.

Manure wastewater is the main waste of animal farming activities. During treatment of such wastewater, there are various factors that can cause concerns such as the generation of methane gas, ammonia, and odor (due to volatile organic acids) [63]. Animal manure wastewater is generally characterized as high strength, rich in various nutrients and phosphates [64–66], and must be treated to meet specific regulations. Alkaline-thermally pretreated swine wastewater seems to be suitable in enhancing MFC operation compared to raw swine wastewater, enhancing resources and energy recovery [67,73].

Animal carcass wastewater can also be a good substrate for MFCs and it is conventionally disposed of after the alkaline hydrolysis; the final sterile solution is a dark brownish alkaline solution characterized by high amounts of BOD (70 g/L),

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COD (105 g/L), ammonia (1 g/L), organic nitrogen (8 g/L), and total phosphorus (0.4 g/L) (Table 12.4) [68].

## 3.5 Landfill leachate treatment

Landfilling is one of the most widely used processes for waste disposal. Leachate is mainly generated from precipitation, surface runoff, and infiltration or intrusion of groundwater percolating through the landfill [69]. It is very difficult to treat leachate wastewater due to the presence of various types of contaminants and high concentrations of recalcitrant and poorly biodegradable materials. Different methods have been used to treat such wastewater including advanced oxidation techniques, membrane processes, biological processes, coagulation-flocculation methods, and so on [70,74]. These methods are effective but they have some limitations, such as lower treatment efficiency and high operational cost. Therefore, to treat leachate wastewater, an efficient and economical treatment process such as application of MFCs is more beneficial (Table 12.5).

Acidogenic food waste leachate, characterized by a complex structure and high organic load, was evaluated as substrate for MFCs [37,38]. Rikame et al. [37] used food waste leachate as substrate for dual chambered MFC with a COD concentration of 5000 mg/L and achieved a very high electricity generation of 15,140 mW/m$^2$ and COD removal efficiency of 90%. The same configuration of dual chambered MFC was used in another study using food waste and obtained very high COD removal (98.7%) and electricity generation (432 mW/m$^2$). Table 12.5 depicts different landfill leachate wastewaters utilized as substrate in MFCs and their performances for electricity generation.

## 3.6 Palm mill oil effluent treatment

Palm oil is one of the most important and high yield crops in tropical countries. During its processing to produce commercial oil, it generates high amounts of palm oil mill effluent (POME), which is characterized by complex substrates consisting of amino acids, inorganic nutrients, and a mixture of carbohydrates ranging from hemicelluloses to simple sugars. After processing 1 ton of palm oil, more than 2.5 tons of POME can be produced [71], with COD and BOD up to 50,000 mg/L and 25,000 mg/L, respectively, but also with high acidic content, which is a cause for environmental concern. There are several conventional methods available to treat POME, but they have their own drawbacks, namely requirement of hydrolysis and highly energy consumption. On the other hand, processing of such wastewater using MFCs can balance energy requirements with power generation [39–41]. Baranitharan et al. [39] used dual chambered MFC to treat POME and obtained a very high power generation of 765 mW/m$^2$, along with COD removal of 32%. In another study, cylindrical MFC was used to treat POME and obtained a high COD removal efficiency (90%) and electricity generation of 765 mW/m$^2$ (Table 12.6).

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## 3.7 Paper and pulp industry wastewater treatment

Paper and pulp industry wastewater contains very high concentrations of soluble organic matter and particulate matter (cellulose). Conventional methods are ineffective to treat such cellulose-containing wastewater, but some agriculture- and bio-based industries are well known for their efficient treatment and resource recovery. Single and two chamber air cathode MFCs has been utilized to treat such wastewater and obtained a good yield of electricity generation, which are 1070 and 880 $mW/m^2$, respectively [43]. Huang and Logan [42] treated paper recycling wastewater in single chambered MFC and obtained COD removal value of 60% and electricity generation of 506 $mW/m^2$. Table 12.7 shows different paper and pulp industry wastewater treatment with different configurations of MFCs.

## 3.8 Petroleum wastewater treatment

Petroleum wastewater is generally generated from refinery effluent or sites contaminated with petroleum hydrocarbons. MFCs have proven to be an effective technique to treat such wastewater (Table 12.8). Studies have been conducted for possible in situ applications using MFCs. One such study was conducted by Chandrasekhar and Venkata Mohan [45] using petroleum sludge as a substrate for MFC and the study reported a power generation of 53.11 $mW/m^2$. Morris and Jin [46] obtained 24% TPH (total petroleum hydrocarbon) removal and 2162 $mW/m^2$ Pd in sediment-MFCs containing TPH. Foad Marashi et al. [47] demonstrated treatment of high organic strength PTA (purified terephthalic acid) wastewater obtained from petrochemical plant in a membraneless single chamber MFC.

Petroleum refinery wastewater with COD concentration of 250 mg/L was treated using dual chambered GC-packing type MFC and results showed a good COD removal (64%) and power generation (330.4 $mW/m^2$). In another study, wastewater of PTA from a petrochemical plant was examined in a membraneless single chamber MFC for the first time and obtained a COD removal of 74% and 31.8 $mW/m^2$ of electricity generation.

## 3.9 Pharmaceutical wastewater treatment

Pharmaceutical industry wastewater is characterized by the presence of complex compounds that are difficult to biodegrade, along with high COD values. Table 12.9 shows some of the selected studies on treatment of pharmaceutical industry wastewater using MFCs. In one study, pharmaceutical industry wastewater comprising a mixture of 1 g/L glucose and 50 mg/L penicillin was fed into an air cathode, single chamber MFC [49,50]. The results obtained showed a very high electricity generation of 101.2 $W/m^2$. Velvizhi and Venkata Mohan [48] investigated recalcitrant pharmaceutical effluents characterized by complex composition and high toxicity as substrate for MFC. The study reported a 68.5% COD removal along with 205.61 m $W/m^2$ power production. Zhang et al. [51] studied paracetamol-containing effluent using a dual

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chamber MFC. Steroidal drug wastewater was fed to MFCs by Liu et al. [52], which obtained a very high energy generation (22.3 $W/m^2$) and good COD removal (82%).

## 4. Conclusion and future perspectives

The promise of lowering total treatment costs while reducing biomass output makes direct electricity recovery from wastewater using MFCs an appealing option for industrial wastewater treatment. From the literature survey it is clear that MFCs have been successfully implemented for treatment of various types of industrial wastewater. MFCs can be designed for portable and in situ applications in addition to delivering more environmentally friendly and easily accessible source of energy. In the past few decades, research and development in this area have gained significant momentum. New research avenues such as application of nanoparticles, conducting materials, etc. in MFCs to improve their performance are being explored. However, more work is still needed to achieve a deeper understanding of the various mechanisms of resource recovery and the economic viability of field-scale MFC technology from the engineering point of view. For example, despite the fact that research efforts over the previous decade have increased power densities by several orders of magnitude, further breakthroughs are needed to enable these technologies for large-scale practical applications.

In this regard, future research should focus on screening of more efficient, toxic resistant electrogenic microorganisms that are capable of utilizing wide range of substrate for their successful use in MFCs for wastewater treatment. In addition, pretreatment of recalcitrant wastewater to make it more biodegradable can also be focused upon, which will definitely help in improving process performance. Cost reducing measures such as reducing the installation, running, and replacement cost of the systems are another important future research direction, as economic effectiveness is one of primary criteria to assess the commercial success of any new technology. The efficiency of energy recovery should also be investigated in depth to prevent any loss of energy during the operation. Moreover, additional attention should be given to integrate MFCs with other existing technologies in order to generate multiproduct platforms in line with the biorefinery concept. This will help in implementing the waste-to-energy concept, which in turn will support creating a circular bioeconomy.

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CHAPTER

# Microbes and wastewater treatment

13

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## 1. Introduction

Availability of clean water is a challenge to the mass people, although clean water is considered as a fundamental human right. The global population is foreseen to explode more than 5 billion by the year 2030 [1]. The dynamic increase of such population is directly linked to water pollution as it has been putting a pressure on available water resources due to high demand and contaminating it with toxic chemicals from the industries along with day to day release of wastes. This, if unchecked, will have adverse effects on public health [1]. As a result of such scenario, it is important that the countries with great economy should invest their proportion of wealth in building the sanitation infrastructure. The large-scale disposal of waste and dumping it into natural water bodies have made their way through the headlines and bulletins of various international media. The wealthy countries are contributing their significant share in constraining the pollution of the population. Water contamination with heavy metals has grown to be an alarming public health-related concern. Moreover, it is very crucial to identify biological, chemical, and physical aspects of contamination and to conduct mandatory treatment plan along with public awareness [2]. The industrial effluent wastes constitute hazardous organic and inorganic pollutants that employ severe pollution in water bodies following soil environment that affects the ecosystem. India, alone contributes to one-third of total agents of global water pollution and about 3.4 million of the global population suffers and dies due to pollution caused by industrialization [3]. Microbes have been used for a variety of products including probiotics, enzymes, and biofuels such as bioethanol, biobutanol, and hydrogen gas. These microbes perform a vital role in the breakdown and removal of nutrients and organic matter in the wastewater and convert them into the substances that are environmentally beneficial. They feed on the nutrients present in the sewage such as nitrogen, phosphorus, sodium, potassium, iron, calcium, and complexes, for example, fats, sugars, and proteins. Intensifying microbial population in wastewater treatment system leads to depletion of organic matter, toxic substances, nutrients, and pathogens. Microbes secreting enzymes mainly cause degradation of organic materials in wastewater and serve as universal catalyst and trigger ecological transformations.



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## 2. Microbial diversity in the treatment of wastewater

Microbes play a crucial role in the wastewater treatment process and are mainly responsible for the biodegradation of organic, inorganic materials and the salvage of nutrients in the natural environment [4]. Bacteria, protozoa, metazoa, algae, and fungi are some of the commonly found microbes present in wastewater treatment, as shown in Fig. 13.1. During the treatment of wastewater, microorganisms not only actively metabolize contaminants but also generate alternative fuels such as bioethanol, syngas, biohydrogen, and biogas.

In municipal wastewater treatment plants, phylum Proteobacteria has been found predominantly (21%–62%). Betaproteobacteria, which is the most abundant class of this phylum, is mainly involved in organic and nutrient removal [5]. The subdominant phyla are Acidobacteria, Bacteroidetes, and Chloroflex [6]. Hence, for planning a biological wastewater treatment system, several aspects of the ecology and dynamics of microbial population should be taken into account. It is important to incorporate theoretical ecology in waste water treatment plant (WWTP) design and operation, since it allows improved prediction of microbial population assembly. Thus, to get a systematic assessment of the microbial population in the wastewater, various biological methods/techniques like denaturing gradient gel electrophoresis (DGGE), terminal-restriction fragment length polymorphism, 16S rRNA gene clone

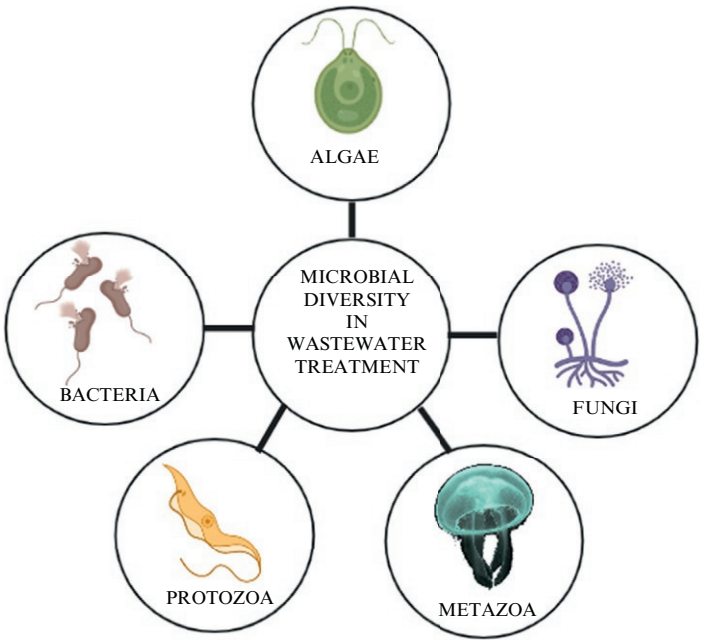


**FIG. 13.1**

Diversity of microbes in wastewater treatment.

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library, and fluorescence in situ hybridization analysis are used. However, the majority of bacteria present in the natural environment cannot be grown on synthetic media in the laboratory [7]; therefore, it is very important to apply these molecular-based techniques to characterize microbial population present in wastewater treatment.

In 16S rRNA sequencing, sequences of genes for the classification and recognition of prokaryotes depend primarily on comparisons to a database of known sequences. A simple yet very robust criterion for the identification of newly isolated strains is provided by the 16S rRNA gene sequence similarity between two strains, whereas phylogenetic analysis can be used to elucidate overall evolutionary relationship between related taxa [8]. 16S rRNA gene sequence analysis provides a reproducible and technically simple process that is also scalable. Different groups of microorganism play different roles in wastewater treatment process. Some of the groups of microorganisms are discussed here.

## 2.1 Role of bacteria

Bacteria play a crucial role in the management of wastewater and are largely responsible for the reduction and alteration of organic compounds in the effluent. The efficiency of the biological treatment of wastewater is determined by bacterial metabolism. By their ability to absorb the metallic ion into their cell walls, they facilitate the elimination of metals. With the help of various metal-binding proteins and peptides such as metallothionein and phytochelatins, microorganisms may absorb heavy metals, e.g., cyanobacteria limit the toxicity of metals by the development of metal-binding proteins. The average bacterial concentration in wastewater treatment is $10^8$–$10^9\,mL^{-1}$. Silva-Bedoya et al. [8] determined 11 bacterial species (*Enterococcus thailandicus, Chromobacterium vaccinii, Serratia* sp., *Kosakonia oryzae, Cronobacter sakazakii, Enterobacter asburiae, Leclercia adecarboxylata, Klebsiella oxytoca, Klebsiella pneumoniae, Bacillus* sp., and *Escherichia coli*) in wastewater released by industries. Some of the *Bacillus* sp. strains have the capacity to formulate a mechanism to relieve the metal stress by an active transport efflux pump.

## 2.2 Role of protozoa

Protozoa play a vital role as predatory activity on pathogenic bacteria in the liquid medium and also play a part in the elimination of organic matter in sewage by digesting them. They are linked to activation of sludge in wastewater treatment with bacteria. In the biological environment, protozoa often maintain good equilibrium by removing excess bacteria, encouraging their growth and promoting floc [9]. In activated sludge, protozoa can mineralize carbon and can remove mineral nutrients as bacteria expedite the carbon supply. The presence of protozoa has been found to increase the rate of nitrification per cell, possibly because of the capability of protozoa to control population of bacteria. Inorganic and organic products are released by protozoa in their surroundings, mainly recycled nutrients like nitrogen,

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phosphorous, and organic carbon. However, it may also contain stimulatory compounds that help to dissolve organic carbon pool and cause effects on bacterial physiology and development [10,11]. In the aeration tanks, ciliated protozoa can reach up to the density of $10^7$ cells $L^{-1}$ and play a crucially important role in the elimination, through grazing [10] the majority of dispersed bacteria, which will induce high turbidity in the final effluent [4]. Different types of protozoa play different roles in wastewater treatment (Table 13.1). Susceptibility of protozoa toward environmental variations is very high, and changes in the protozoan population are known to influence the whole food chain of these artificial ecosystems; therefore, the biological efficiency of wastewater treatment plants is affected. In this reference, the application of Sludge Biotic Index (SBI) was recommended by Amaral et al. [12], who focused on the protozoan community's abundance and diversity in the activated sludge aeration tank. The SBI can range from 0 as the worst condition being indicated up to 10 as the most desirable condition being indicated. Numerical assessment helps to compare different sludges or sludge biological consistency over time. Typical protozoan concentration in aerobic activated sludge ranges from $5 \times 10^3$ to $2 \times 10^4$ [4]. Some of the ciliated protozoan species typically found in effluent treatment plants are *Chilodonella uncinata, Opercularia coarctata, Trachelophyllum pusillum, Vorticella microstoma, Carchesiumpolypinum,* and *Aspidisca costata* [13].

## 2.3 Role of metazoa

In general, metazoa (such as rotifers, tardigrades, and nematodes) are multicellular eukaryotic species whose size is greater than other protozoa and are generally found in wastewater. In activated sludge, the concentration of metazoa is generally very low ($10^3\,mL^{-1}$), but they are helpful in evaluating the conditions like sludge age, organic load, aeration, and retention time of the treatment systems. There are various types of metazoan that were helpful in characterizing and monitoring different aerobic wastewater systems and diagnosing operation conditions such as BOD or COD, nitrogen utilizing efficiencies, and foaming phenomena of activated sludge in wastewater treatment plant. For instance, Tardigrada, type of metazoa, that are small invertebrates with elongated and cylindrical body, having wide ecological tolerance, which makes them suitable to inhabit the activated sludge, are used as indicators of pollution level. Jakubowska-Krepska et al. [14] reported that the tardigrades are potential bioindicators, and they indicate higher pollution levels and the high

**Table 13.1** Different protozoa and their roles in wastewater treatment.

| Type | Function |
|---|---|
| Flagellates | Nourish and flourish on organic particles present in wastewater |
| Ciliates | Eliminate floating bacteria and help to clean the effluent |
| Crawling ciliates | Indicator of good treatment |
| Sessile ciliates | Dominate at the end of the process |

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amount of suspended solids in wastewater, whereas rotifers enhance clarification of effluent by producing a sticky substances that aid in flocs formation. Nematodes are majorly found in trickling filters and older sludges. However, their population generally decreases in wastewater as its temperature increases. In addition, they are sensitive to anoxic conditions [15]. Wastewater effluent also contains Cladocera and Copepods. Cladocera consume algae and bacteria present in wastewater [16], while Copepods thrive in water with high dissolved oxygen (DO) and low bacterial population [17].

## 2.4 Role of algae

Microalgae have the ability to perform photosynthesis and can transform solar energy to biomass and have developed the efficiency to consume nutrients such as phosphorous and nitrogen in a short period of time. Species of algae that are widely found in the industrial wastewater treatment process include *Euglena, Oscillatoria, Synechocystis, Microcystis, Lyngbya, Chlamydomonas, Phormidium autumnale,* and *Limnothrix*. These microalgae can be used for the treatment of a wide variety of wastewater systems and are known to be a tertiary treatment method that removes organic ions. In addition, algae also remove radioactive compounds present in the wastewater by accumulating such substances in their cells. For instance, spirogyra can acquire radioactive phosphorus by a factor of 850,000 times from water as highlighted by Vetrivel et al. [18]. Mahapatra et al. [19] analyzed the treatment efficiencies of the algae-based sewage treatment plant in Mysore. The study revealed modest levels of treatment, with 60% total chemical oxygen demand (COD) elimination, 50% filterable COD removal, 82% total biological oxygen demand (BOD) removal, and 70% filterable BOD removal. The efficiency of nitrogen removal was very less. However, after higher *Euglena* cells growth, a rapid decrease in the suspended solids occurs, which indicates particulate carbon removal by algal ingestion.

## 2.5 Role of fungi

In biological wastewater treatment, fungi have many benefits over bacteria being a source of useful fungal by-products such as lactic acids, amylase, and chitinase. Fungi contain a group of extracellular enzymes that promote the biodegradation, by nonspecific oxidation reactions of refractory compounds such as dyes, phenolic compounds, and polyaromatic hydrocarbons (PAH) [20–22]. By increasing their bioavailability and conversion into less toxic forms, fungi play a potential role in heavy metal remediation. *Penicillium, Aspergillus*, and *Rhizopus* have been found to be involved in eliminating heavy metals from wastewater [23]. Some fungi have the ability to bind metals, such as *Klebsiella oxytoca, Allescheriella* sp., *Stachybotrys* sp., *Phlebia* sp., *Pleurotus pulmonarius*, and *Botryosphaeria rhodian* [24]. In an environment of low pH, they have the ability to breakdown organic matter and oxidize ammonia into nitrite and nitrate where bacterial growth is prevented.

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The *Verticillum terrestre, Hymenoscyphus ericae,* and *Neocosmospora vasinfecta* fungi display resistance to Hg and the ability to transfer Hg (II) to a nontoxic form of the toxic state [25]. The enzyme-mediated operation that provides the solution for the treatment of waste streams containing dangerous or xenobiotic organic contaminants is one of many advantages of the fungal process. Relevant and unspecific extracellular enzymes secreted by fungal biomass degrade the complex organic contaminants of large molecular mass. For example, through nonspecific oxidation reactions, the extracellular enzymes secreted by white rot fungi catalyze polycyclic aromatic hydrocarbon (PAH) degradation, contributing to the development of quinone varieties and hydroxylated aromatic compounds [26]. In addition to the development of extracellular enzymes, fungi play a major role in toxic compound biosorption during wastewater treatment.

## 3. Characteristics of wastewater

Wastewater is typically distinguished by physical characteristics (color, odor, and turbidity), chemical characteristics (pH and alkalinity), COD, BOD, total dissolved solids (TDS), total suspended solids (TSS), total DO, total organic carbon (TOC), nitrogen, phosphorus, volatile solids (VS), fats, oil and greases, and conductivity. Mostly wastewater contains various chemical, biochemical, and other objectionable matter that ranges from source to source it is collected. There are so many sources of wastewater such as domestic wastewater, sewage sludge, food wastewater, paper industry wastewater, textile wastewater, and pharmaceuticals wastewater. A large number of hazardous chemicals and heavy metals, such as nickel, lead, cadmium, antimony, arsenic, mercury, zinc, and copper, are found in effluents released from industries. Household wastewater holds lower levels of chemicals than commercial wastewater, but the level of organic matter is high, whereas agricultural wastewater contains high levels of chemicals like pesticide, weedicide, manure, etc. and biological substances such as algae, fungi, and bacteria. Wastewater, along with several gases, consists of 70% organic compounds and 30% inorganic compounds. Organic compounds are primarily sugars, fats, and proteins, while heavy metals, nitrogen, phosphorus, sulfur, chloride, etc. are inorganic matter. Dissolved gases typically found in wastewater include hydrogen sulfide, methane, mercury, oxygen, nitrogen, and carbon dioxide.

The constituents of wastewater have a major effect on the treatment method to be taken, as well as the specification process for the reactor configuration. For characterizing wastewater, the most important factors are concentration of suspended solids, quality of organic matter (BOD or COD), temperature, pH, and presence of inhibitors [27]. Several reactor designs can be affected by suspended solids and the aggregation of grits. Liquid waste or wastewater is known to have a concentration of suspended solids below 1000 mg/L with minimal amounts of grit, mostly eliminated by quick pretreatment (inorganic nonsoluble solids). The concentration of suspended solids in wastewater is the defining measure for grading wastewater purity in

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low, medium, and high grades. In wastewater, the concentration below 1000 mg/L falls in low grade, 1000–10,000 for medium, and 10,000–200,000 for high grades. These wastes include different sources such as industrial, food processing, and other production wastes.

## 4. Methodologies used for wastewater treatment

Different kinds of pollutants found in the wastewater may be eliminated by employing various methods as shown in Fig. 13.2. Based on the source of wastewater, different treatment approaches are used. There are generally three stages involved in wastewater treatment: primary, secondary, and tertiary [28]. Primary treatment will decrease BOD by 20%–30% and suspended solids up to 60% [29]. The removal of oil, grease, fat, sand, and coarse solids is included in this stage.

BOD and TSS can be reduced by up to 85% by secondary treatment. This process entails the degradation of the dissolved contents of the sewage by the mechanism of biological degradation. The last stage in secondary treatment is to remove biological matter along with very low amount of remaining organic material and dissolved solids from the treated water. Up to 99% of sewage impurities can be eliminated by tertiary treatment. Until discharging the stream, certain operators apply chlorine as a disinfectant. Tertiary treatment is often performed to remove nitrogen and

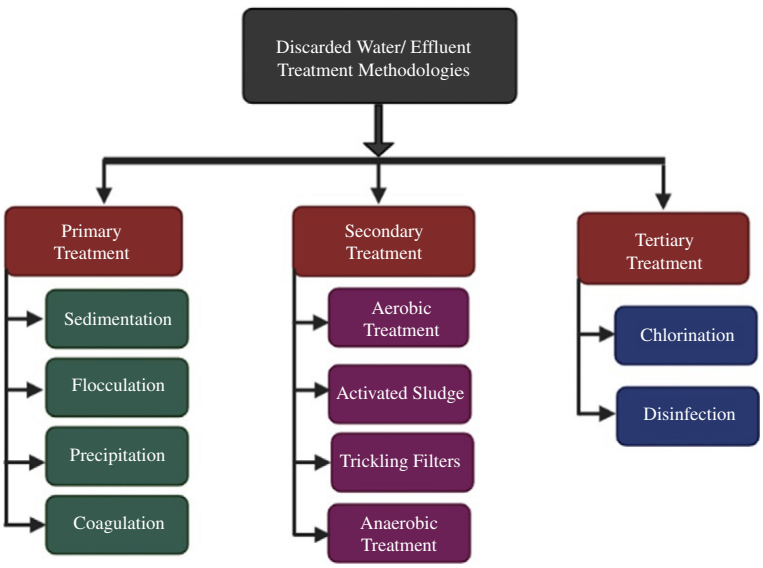


**FIG. 13.2**

Different wastewater treatment systems.

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phosphorus. To better remove or discard toxins or unique substances, tertiary treatment requires specialized devices and technology.

## 4.1 Primary treatment

Primary treatment involves removal of floating and settling materials, such as suspended solids and organic substances. This degree of treatment uses both physical and chemical approaches [30]. Chemical unit processes are often used during physical operations and can be used with biological treatment processes. Chemicals are added to wastewater during chemical processes to bring about changes in its quality. Examples: Regulation of pH, coagulation, chemical precipitation, and oxidation. To make wastewater pH neutral, NaOH, $Na_2CO_3$, $CaCO_3$, or $Ca(OH)_2$ are added in case of acidic wastes (low pH) and $H_2SO_4$, HCl in alkali wastes (high pH). To enhance the attraction between fine particles, chemical coagulants such as $Al_2(SO_4)_3$ (also called alum) or $Fe_2(SO_4)_3$ are applied to wastewater so that they come together to form larger particles called flocs [31]. A chemical flocculent (usually polyelectrolyte) strengthens the mechanism of flocculation by pulling particles together to create larger flocs, which settle faster.

## 4.2 Secondary treatment

After primary treatment, secondary treatment is done to remove the dissolved materials or particulate matter present in wastewater. It is accomplished by various biological methods such as aerobic treatment, activated sludge method, trickling filters, and anaerobic treatment [31]. We can employ either one or combination of methods depending upon the source and nature of wastewater.

### 4.2.1 Aerobic treatment

Aerobic treatment is used to eliminate traces of organic volatile compounds (OVCs) in wastewater [32]. It is also used in transferring of oxygen present in a gas phase into wastewater through a process called "gas adsorption" or "oxidation" for an oxidation of iron or manganese. Aerobic treatment also aids in the escaping of dissolved gases such as hydrogen sulfur and carbon dioxide. It also helps in reducing ammonia, nitrous oxide, and methane. Aerobic treatment can be done through oxidation ponds or aeration lagoons. The major disadvantage of this method is that it cannot treat wastewater containing high amount of biodegradable matter.

### 4.2.2 Activated sludge method

The activated sludge system is focused on a combination of dense bacterial communities dispersed under aerobic conditions in wastewater [33]. This method is inexpensive and widely used. The activated sludge process involves five independent parts, i.e., bioreactor, sedimentation tank, activated sludge, aeration and mixing system, and returned sludge [34]. Higher rates of respiration and bacterial growth can be achieved when there is unlimited supply of nutrients and oxygen, which results in

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the degradation of organic matter that is present in wastewater and biosynthesis of biomass. However, this method produces huge quantity of sludge that puts extra economic and environmental burden. Hence, more advancements are required.

### 4.2.3 Trickling filters

The trickling filtration system is similar to the activated sludge technique, only that instead of being suspended, the microorganisms employed to stabilize the biological waste material are bound to a fixed bed. In general, filters involve a vessel filled with inert media (lava, slag, gravel, rock, coke, ceramic, polyurethane foam, plastic media, and sphagnum peat mossor plastic media). To sprinkle, wastewater system is used, and the sprinkled wastewater trickles under the influence of gravitational force through media supporting biomass. Slime layer usually formed on the media and the microbes absorb dissolved organic matter for their maintenance and proliferation because of the cascade of wastewater via spaces in media [35].

### 4.2.4 Anaerobic treatment

Biodegradation of organic waste into methane and carbon dioxide in the absence of oxygen is the basic principle of anaerobic treatment process. This method is generally employed when there is high quantity of biodegradable organic matter with BOD $>500$ mg/L present in wastewater such as wastewater from food processing and agricultural industries [36]. During the process, there is coordinated and sequential activity performed by various microbes (archaeal and bacterial), which includes hydrolysis, acidogenesis, acetogenesis, and methanogenesis to convert the complex organic macromolecule. For desired microbial activity, highly efficient anaerobic digestion reactors are required that are maintained in the mesophilic or thermophilic temperature range for the application in the WWTP.

## 4.3 Tertiary treatment

The final cleaning process that enhances the quality of the wastewater before discharging it to the environment is the tertiary treatment. In this step, inorganic compounds like phosphorus and nitrogen and contaminants like parasites, bacteria, and viruses, which can be a threat to public health are removed. Alum is generally used to remove extra particles of phosphorous as well as to remove all the remaining solids present in the filters. By killing all microorganisms in treated wastewater, chlorine tank disinfects the tertiary treated wastewater. The excess chloride is eliminated by the addition of sodium bisulfate before discharging to the environment.

# 5. Role of 16S rRNA in the classification of microbes

Microbial biodiversity is being extensively studied by the cloning and sequencing of 16S rRNA gene [37]. This is one of the most recent approaches to analyze and characterize microbial diversity, hence finds application in wastewater treatment.

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This method follows the following steps [6]: (1) The nucleic acid extraction from the microbial sample. (2) To produce a mixture of rDNA copies of microorganisms, polymerase chain reaction (PCR) amplification of the 16S rRNA is done by using universal primers for bacteria or archaea. (3) Cloning of the PCR products into a sufficiently high number of plasmid copies and then transforming the *Escherichia coli* competent cells with this vector. (4) Transformed clones are selected on the basis of indicator present in the plasmid. (5) From the clones, the extraction of the plasmid DNA is done. (6) The clone library is created by sequencing of the cloned genes. (7) Finally, various phylogenetic softwares are used such as ARB, Seqlab, PAUP, and PHYLIP to identify and affiliate the isolated cloned sequence. The microbial composition of textile wastewater treatment plants has recently been assessed by Numberger et al. [38] in comparison of municipal wastewater treatment plant microbial populations using pyrosequencing technique in an attempt to understand the key microbes that perform well in purification of textile wastewater. Their research showed more abundant nitrifying and denitrifying bacteria and those involved in phosphate accumulation, whereas sulfur reducing bacteria were found in textile wastewater plants. Do et al. [39] also provided a study of the microbiome of effluent. They have used Illumina MiSeq 16S rRNA gene amplicon sequencing and used Calypsco for microbiome analysis. They found that proteobacteria, bacteriodes, actinobacteria, firmicutes, tenericutes, and verrucomicrobia are present in high number in different wastewater samples. Their work has provided a better understanding of the bacterial communities in the wastewater. Another study also characterized different bacterial communities in wastewater by using full-length 16S rRNA sequencing. This study was helpful in the characterization of harmful and pathogenic bacteria that are required to access health risk [39]. 16S rRNA technique is fast and reliable method to identify microorganism in wastewater. This method helps us to understand how the performance of bacteria impacted in WWTP by identifying it by the procedure mentioned above [40].

## 6. rDNA technology for wastewater treatment

This technology allows copies of DNA to be produced that can be combined precisely at the desired location on a genomic or plasmid DNA. The combination is called a hybrid of recombinant and genomic DNA. A hybrid DNA, for the most part, is a replica of one or more genes that can be expressed in a new host organism known as a recombinant clone. Using this procedure, certain clones may express the properties of foreign genes that are acquired. This technology is today's most effective biotechnological tool that is being pursued through bioremediation in numerous fields, including environmental pollution management and wastewater treatment [41]. Li et al. [41] investigated the role of recombinant bacterium for the improved treatment of acetonitrile-containing wastewater. They showed that formation of biofilm by nitrile degrading recombinant *Bacillus subtilis* N4-pHT01-*nit* was potentially able to completely degrade the initial concentration of acetonitrile

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(800 mg/L) within 24 h in a moving bed biofilm reactor (MBBR). Another approach to improve wastewater treatment is the use of genetically modified microorganism (GMO) [42]. GMO involved in wastewater treatment is transfected with genes that encode catabolic enzymes involved in pollutant biodegradation, increasing the efficiency of biodegradation by microorganism. Genetically engineered *Escherichia coli* has been evaluated for atrazine and direct Blue 71 dye biodegradation in wastewater [43]. There are many advantages to genetic engineering through recombinant DNA technology over natural isolates. The technology facilitates the design and growth of microorganisms capable of functioning effectively through multiple degradation pathways to degrade even previously nonbiodegradable compounds partially or completely. It may be preferable to develop recombinant microorganisms with the ability to degrade xenobiotics over consortiums of natural isolates.

## 6.1 Elevating the rates of biodegradation using rDNA technology

Recombinant DNA technology is now being tested to further increase the rate of biodegradation multiple times by judicious use of GMOs and mediators created by this technology. In addition, it offers useful resources to track bioremediation, along with other molecular biology strategies such as random amplification of polymorphic DNA (RAPD), fluorescent in situ hybridization (FISH), DGGE, and CRISPR/Cas9 by assessing the population composition before and after and factors that influence the survival of the bacteria involved in the process.

### 6.1.1 Random amplification of polymorphic DNA

This approach is based on random amplification of components of polymorphic target DNA using short primers. In agarose gel electrophoresis, the randomly amplified fragments of DNA are then compared. It is useful for species-specific pattern recognition and requires very limited quantity of sample of DNA. PCR-RAPD has been used to test DNA isolated from root meristem onion cells (*Allium cepa*) exposed to growing concentrations of hospital wastewater [44]. The wastewater from hospital leads to genotoxic effect and at lower concentration it affects DNA. Thus, RAPD is a useful tool for genotoxicity estimation in meristem root cells of *Allium cepa*.

### 6.1.2 Fluorescent in situ hybridization

It is a molecular probing procedure used on chromosomes to detect the presence or absence of particular DNA sequences. This approach uses fluorescent probes that attach to sections of the chromosome with a high degree of sequence similarity. Boon et al. [45] studied the application of fluorescence in situ hybridization for the study and characterization of nitrifying bacteria in nitrifying/denitrifying wastewater treatment plants and concluded that already existing bacteria that are causing the oxidation of ammonia to nitrate are majorly *Nitrospira* spp., which is ammonia oxidizing β-proteobacteria.

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### 6.1.3 Denaturing gradient gel electrophoresis

It is a type of molecular fingerprinting. This technique takes melting point into consideration and distinguishes on the basis of base substitutions. It involves the separation of DNA fragments using these parameters. It is useful for comparing the polymorphic DNA fragments' melting actions and for identifying fragments that have mutations. This technique is used to characterize microbial diversities and their functional genes at wastewater contaminated sites [46].

### 6.1.4 CRISPR/Cas9

It is a new breakthrough genome editing method that offers a robust and multiplex genome editing tool. The clustered rapidly interspaced short palindromic repeats (CRISPR)/Cas help researchers to precisely control unique genomic elements [47]. CRISPR/Cas9 technology can be employed in wastewater treatment in two ways. Screening and modification of genetic alga strains at particular pollution sources and genetic engineering and expression of antifouling ingredients from *Dunaliella salina* [47]. In different biological, geographical, and environmental settings, the techniques of molecular biology and recombinant DNA technology have unleashed the microbial diversity and population dynamics of the microbial ecosystem in wastewater.

## 7. Technology for microbial electrical remediation

Due to human activities and rapid industrialization, a large volume of metal-laden wastewater is generated. Because of radioactive potential and carcinogenic effects, the tainted metal(loid) water faces great health and environmental risks. Stringent standards have been adopted for the discharge of different metal ions in wastewater in order to prevent environmental pollution. An ideal method of treatment is not to clear the metals but to extract and recover them during the treatment period. The method of activated carbon-based adsorption, ion exchange, and membrane technology for the treatment of vast quantities of industrial effluent are decidedly expensive, and these methods cannot be used at large industrial scale with a low number of heavy metal ions [48–50]. Hence, a study on new, appropriate, and cost-effective metal removal methods from water has also recently become a field of intensive research. Bio-electrochemical systems (BES), and particularly microbial fuel cells (MFCs), have evolved in recent years as a modern remedial solution used to mobilize contaminants to recover or reduce in the subsurface. The technology is enabled by bioelectrocatalysis to process and recycle wastewater because algae, bacteria, fungi, and yeast can minimize and dispose of metal ions. Interestingly, wastewater containing heavy metals can be treated in both the anode and cathode chambers of MFCs [49,51,52]. The basic principle behind the approach is that the biological transfer event at the positively charged electrode (anode) is used by using them as terminal electron acceptor to transport electrons to the negatively charged electrode (cathode) and accelerate reduction with metal(loid) precipitation. Therefore, BES provides a

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new, optimized wastewater treatment platform for oxidization and reduced energy, water and metal(loid) recovery reactions. MFCs take one step forward from other technology of waste management, through the traditional MFC function, to recover metal species. If toxins are used as electron acceptors inside the cathode chamber of the MFCs, the environmental benefits of MFCs could be increased.

## 8. Conclusion

The alarming rates of water pollution have become a major topic of concern because of water scarcity in major parts of the world. The engrossed idea of treating wastewater in order to get this under control has given us a hope to reincarnate the available water resources. There have been truckloads of programs and research projects for the enhancement and treatment of available water resources by the governments all around the world. These involve many methodologies from basic chemical analytics to the complex bioengineering processes. Most of the treatment plants have constantly been using microbial resources for bioaugmentation into wastewater treatment systems due to their environment friendly nature and better efficacy over the chemical compounds. Many of the bacterial and archeal species are modified using genetic engineering technologies like FISH, DGGE, and CRISPR/Cas9 technology to develop highly enhanced and environment friendly generations of GMOs. Also, the evolving advancements in bioinformatics have proven to be very helpful in the identification, classification, and characterization of newly discovered and already existing microbial species. Some of the softwares such as ARB, Seqlab, PAUP, and PHYLIP that can be used for the depository and computational analysis of the sequences available or through the next-generation sequencing technology provide a very comprehensive approach in the direction of identification and modification of both the pathogenic as well as environment friendly species. All of these techniques should be used collectively as a cumulative vision for wastewater treatment. Hopefully, in the near future, we would be able to develop more proficient ways to tackle this pandemic of water pollution and step forward to a healthy lifestyle with the help of these scientific approaches.

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## Conflict of interest

The authors declare that they have no conflict of interests.

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CHAPTER

# Challenges in the scale-up of MES for wastewater treatment

14

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## 1. Introduction

The greenhouse effect resulting in global warming, which is mainly induced by the accrual of gases such as $CH_4$, $CO_2$, and $N_2O$ within the atmosphere, has become a serious challenge: in particular, $CO_2$ represents most of the greenhouse gas (GHG) emissions, which break down as 3% $N_2O$, 24% $CH_4$, and 63% $CO_2$, marking $CO_2$ as the major cause of global warming [1]. Annual $CO_2$ emissions have shown a constant growth inclination since 1971, rising sharply from 14.1 gigatons in 2014 to 38.2 gigatons in 2017 [2]. Under the Paris Agreement, it was agreed that global temperature rise will be kept within 2°C to achieve global carbon balance, and that effective control of $CO_2$ emissions and phasing out of atmospheric $CO_2$ concentrations are priorities for research and technology development over the current decade [3]. To combat global warming, three techniques are purportedly proposed: (1) lowering fossil fuel consumption, (2) creating low-carbon renewable energy sources, and (3) $CO_2$ mitigation technologies such as carbon capture and storage (CCS) and carbon capture and utilization (CCU) [4].

It has been agreed that renewable energy can now partially replace the use of fossil fuels [5]. Developing creative solutions to lower $CO_2$ levels in the atmosphere and reach "zero" $CO_2$ emissions, on the other hand, remains a major challenge. Several CCU technologies have been developed for converting waste $CO_2$ into valuable resources. This illustrates how our perception of $CO_2$ will change if we use it as a resource as part of a circular economy. In contrast to CCS, CCUs may switch



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between catalytic and biological $CO_2$ in large industrial settings, which efficiently adsorbs $CO_2$ and converts the waste emissions to potential resources [6]. In the contemporary $CO_2$ economy, it has become a viable option for the production of a variety of chemical products globally. The conversion of $CO_2$ to monocarbon molecules, especially CO or $CH_4$, has been extensively researched utilizing thermal/electrocatalytic $CO_2$ reduction, generally employing metal-based catalysts [7–10]. Long-chain hydrocarbons can be made using CO and/or methanol mediators [11,12], but new strategies for catalytic long-term stability and unique energy savings are still being researched.

The conversion of biological $CO_2$ to value-added chemicals has been deemed a cost-effective strategy to build a circular carbon economy to successfully reduce human dependence on fossil fuels [13,14]. The use of a raw bioelectrochemical system (BES) for wastewater treatment and resource recovery has been proposed [15]. Microbial electrosynthesis (MES) is a biocatalyst that has been specifically developed to self-retain chemolithoautotrophs and can used as a cost-effective biocatalyst to reduce negative electrode $CO_2$ and produce a variety of products [1,2,5,14,15]. This method, unlike microalgae-based photoreactors, creates organic compounds with relatively short carbon chains for thermal/electrocatalytic $CO_2$ reduction that do not have the problem of removing lipids from microalgae cells. You won't have to deal with an unstable catalyst. MES has become a potentially scalable technology for $CO_2$ utilization in the circulating bioeconomy and high-value biofuel production due to the long-term stability of MES reactors and the high Coulomb efficiency of $CO_2$ reduction in products [13,15]. The MES of acetic acid in $CO_2$ [16] has recently been explored, reaching a high production rate of $685 \pm 30$ ($g\,m^{-2}\,day^{-1}$) [17], or even more by other reports, nearing the lower limit of acetic acid concentration in commercial vinegar [16]. This demonstrates the enormous potential of MES technology in the food business for converting $CO_2$ into value-added biochemicals [16]. Aside from acetate, the MES system can produce more valuable bioproducts such as butyric acid [18], caproic acid [18], and polyhydroxy butyrate (PHB) [19,20]. The vast array of biochemicals created from $CO_2$ in MES provides another strategic plan in materials and chemical synthesis, potentially positioning biotechnology, particularly MES, as a viable supplement to the circular biological economy.

The composition of the reactor, the electron transfer mechanism, the electroautotrophic and mixotrophic microorganisms, and cathode materials used in the MES have all recently been evaluated in prior works [21–23]. Furthermore, some challenges remain unaddressed, such as high energy input and suppression of end-products with low $CO_2$ utilization efficiency, limiting the low-cost production of volatile fatty acids (VFAs) from large-scale $CO_2$ [24]. Bioengineering of microorganisms reduce energy input, improve bacterial colony formation, provide cost-effective electrode materials for superior $CO_2$ mass transport and bioproduct extraction, and indicate the feasibility of biotechnology for achieving circular bioeconomy. It is critical to work with MES to create a setup [24]. The examination begins with a discussion of common anode materials used in MES. The anode is essential for lowering the amount of energy required for anodic breakdown. As a result, a

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thorough investigation of MES cathode materials and configurations for the growth of chemosynthetic autotrophs and the creation of various VFAs is undertaken. The effects of direct gaseous $CO_2$ administration on pH control and $CO_2$ mass transfer at the cathode surface are investigated extensively. An anodic cathodic biocatalyst and bioproduct extraction are included in the energy consumption study of MES. Finally, in the context of turning MES into viable recycling bioeconomy technologies, proposals for optimizing MES systems to reduce overall energy usage and boost VFA output are discussed.

## 2. MES: Anode tuning for efficient electron generation

MES for $CO_2$ reduction is an electrically driven biological microorganism-catalyzed manufacturing method. A proton exchange membrane separates two main compartment anode chambers and a biocathode chamber in a typical reactor layout, as depicted in Fig. 14.1. Most MES research now focuses on cathode $CO_2$ reduction using various microbial inoculums and cathode materials as well as combinations [18]. Microbial catalysis has been shown to be viable for cathodic $CO_2$ conversion to acetic acid at low voltage versus a low cathode potential. When compared to the normal $CO_2$ redox potential, the standard hydrogen electrode (SHE) is 110 mV (−0.29 V vs. SHE) [25]. However, to boost current density and acetic acid production, an applied voltage of at least 3 V is usually necessary, and most scientists assume that water splitting is triggered from the MES anode to the bias [2,16,18,25]. Water-based OER

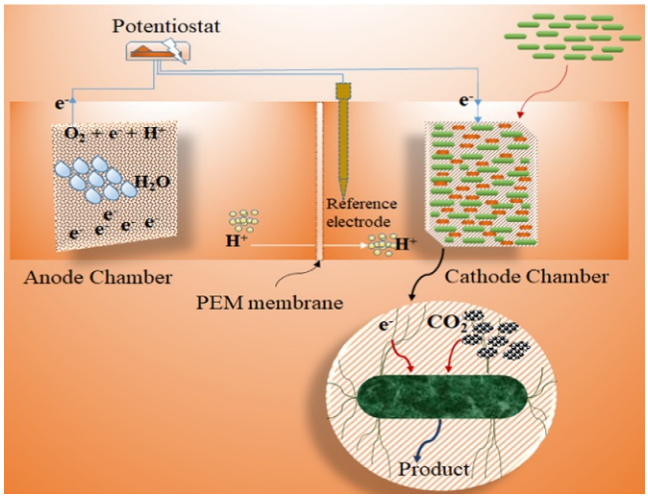


**FIG. 14.1**

Scheme showing microbial electrosynthesis (MES) cells driven by different energy sources. PEM, proton exchange membrane.

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(oxygen evolution reaction) is commonly utilized in MES to generate protons and electrons from the anode [2,16]. Because the reaction is not kinetically beneficial, OER requires a lot of electricity, and it looks to be considerably more complicated than the hydrogen generation reaction (HER) at the negative electrode, which involves 4-electron transfer [2,18,26]. Despite their importance, however, the development of effective MES anodes has received little attention in MES research. Carbonaceous materials such as graphite sticks [25,27], graphite plates [28], and carbon crosses make up the majority of MES anodes [29].

The carbon electrode, on the other hand, exhibits more distinct electrocatalytic OER activity (>600 mV) for driving a current density of 5 mA $cm^{-2}$ [30]: Following tactics have been implemented to minimize excessive energy input and lower the cost of the OER anode applied for MES [30] (i) A tiny quantity of stable noble metal catalyst is placed on the nonprecious metal electrode for efficient OER, as illustrated in Fig. 14.2; (ii) employment of a photoanode; (iii) the use of an anode reaction other than OER for electron generation; as well as (iv) biological anodes for the oxidation of organic or sulfide compounds. Instead of carbonaceous materials, multiple metal electrodes can be employed as MES anodes to generate a superior OER. Metal anodes made of Ti and Pt are said to efficiently drive OER and preserve long-term MES performance without corrosion [31]. Small amounts of noble metal catalysts (Ir or Pt) are placed on inexpensive substrates to function as MES oxides because noble metal electrodes are usually more expensive than carbon [31].

Biosynthetic reduced graphene oxide (rGO) doped with transition metals utilizing electroactive bacteria is described as having a potential application in MES developed for OER with long stability to further lower the cost of catalyst manufacturing. Moreover, because the current MES research focuses mostly on biocathodes with chemosynthetic autotrophs for $CO_2$ reduction, no results on the anode OER overvoltage of this MES anode with noble metal catalysts have been reported, indicating long-term stability. It is a difficult task. Light energy, which is one of the most plentiful renewable resources, can also be employed at the anode to overcome

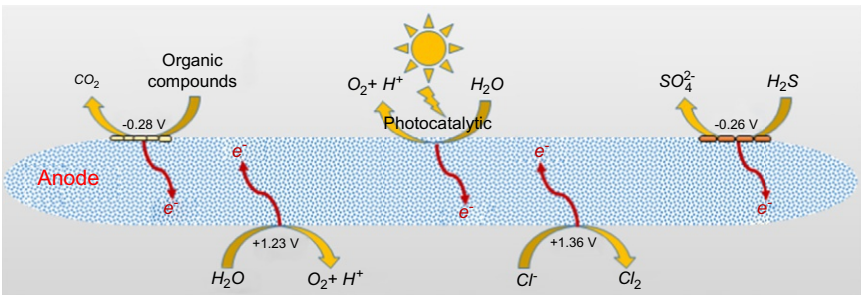


**FIG. 14.2**

Schematic illustration of diverse anode approaches in MES towards lowering energy input. These values are based on the standard redox potential (vs. SHE) of the diverse anodic responses designed for electron generation.

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the OER's overvoltage in the MES and produce "artificial photosynthesis" [32–34]. Recent photoelectrochemical (PEC) devices for hydrogen production via water splitting have been widely documented [35,36]. In this regard, Liu is using titanium dioxide ($TiO_2$) nanowire arrays as light absorption and OER catalysts for MES [4], as are Fu et al., to efficiently absorb solar energy [32]. In the absence of external bias, the instantaneous photoresponse at the MES light anode generates a current of roughly 1.2 mA, proving the practicality of the photo-assisted MES's minimal energy input [32]. As a result, it is hoped that solar energy will be used in MES to achieve both efficient OER and energy input savings. Within a two-chamber MES reactor, oxygen has been reported to diffuse from the anode to the cathode [37]. Oxygen diffusion through ion exchange membranes has been demonstrated to have a negative impact on MFC performance and evolution in previous investigations utilizing two-chamber MFCs [38]. The chlorine evolution reaction (ClER) could be used instead of OER to reduce the energy input and diminish the influence of oxygen incursion on chemosynthetic autotrophic enrichment. At the anode, the electrochemical production of chlorine and oxygen gases happens thus [39]:

$$2Cl^- \rightarrow Cl_2 + 2e^-, E^o = 1.358V \text{ versus SHE} \quad \text{(i)}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E^o = 1.229V \text{ versus SHE} \quad \text{(ii)}$$

When the standard potentials of reactions (i) and (ii) are compared, it is obvious that OER has a lower activation energy than ClER. In electrical convection catalysts, however, better ClER selectivity compared to OER has already been observed, as it has a kinetic advantage over only two electrons involved in chlorine evolution.

Finke and colleagues developed a $TiO_2$ electrocatalyst produced by atomic layer deposition (ALD), which was used to investigate the activity of oxygen and chlorine evolution [40]. ClER had a greater current density (700 mV, 700 mV) than OER (900 mV, 0.05 mA/cm$^2$) after 10 ALD cycles using an identical fluorine-doped tin oxide (FTO) electrode coated with $TiO_2$. The development of cost-effective anode materials for efficient ClER OERs in MES is appropriate to achieve this circulation, given the much lower overvoltage that initiates ClER and the vast market size (50–60 million tonnes/year) of chlorine gas [41]. The biological circular economy could offer an alternative. The bioanode is often used in wastewater treatment to remove chemical oxygen demand (COD), which involves the creation of electrons and protons in BESs like MEC. It has been established that an applied voltage as low as 0.7 V is adequate to drive HER in MEC, despite the fact that this voltage is insufficient to drive OER and HER in MES [42]. The low potential created at the bioanode by oxidation of organic matter is the main cause of this low voltage.

Seeing the wastewater digested from AD usually contains high-strength persistent organic matter [43], combining the bioanode and biocathode of MES for AD wastewater treatment and upgrading of biogas to enhance the role of AD in the circular bioeconomy and replace the anode OER reaction to provide energy input to MES has been proposed [17,42]. The use of bioanodes in MES reactors with bipolar membranes has recently been reported [44,45], although the precise information on

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the anode potential was not presented in some cases. According to another study, the bioanode potential might be decreased to −0.2 V when compared to SHE due to the creation of larger current densities of electrons and protons than the abiotic anode of MES [46]. The integration of bioanodes into MES systems for wastewater treatment and reduction of the energy input was demonstrated in both investigations, with COD removal efficiencies of 45% or higher and Coulomb efficiencies of 60% or higher. Some reduced inorganic molecules (e.g., $S^{2-}$, $HS^{-}$) are anodized in addition to the creation of electrons by organic oxidation at the bioanode [29], undervoltage with the ability to operate as an electron donor. Microorganisms transform sulfides into sulfur while also producing electrons to minimize anodic overvoltages in situ in BES [47,48]. According to Ni et al., the electrochemical oxidation of $S^{2-}$ is as follows [49]:

$$HS^{-} \rightarrow S_s + 2e^{-} + H^{+}, E_{anode} = -0.262 \text{ versus SHE } (pH = 9; 1 \text{ M } Na^{+}) \quad \text{(iii)}$$

The oxidation of sulfides is clearly more beneficial thermodynamically than OER and ClER, as discussed above. Recent research has demonstrated that bioanodes inoculated with sulfide oxidizing bacteria (SOB) with sulfide at an anode potential of 305 or 503 mV vs SHE, can produce sulfide at an anode potential of 305 mV [50]. Electron transport is demonstrated. SHE sulfur drives MES process with 503 mV units, and successful SOB inoculation (*Desulfobulbus propionicus* and *Desulfuromonas*) with bioanode [28], which has been proven to be successful [49].

## 3. MES cathodes for utilization of $CO_2$ as a source for diverse chemical manufacture

The MES cathode, as the key platform for $CO_2$ recycling and biochemical production, is at the heart of the MES system. The choice of the positive electrode material to manage electrical activity and biocompatibility is one of the most important elements impacting the chemical generation of $CO_2$ in MES. For $CO_2$ reduction in MES, a chemically stable negative electrode with low cost, high conductivity, good HER function, and a large biocompatible surface area for cell adhesion/biofilm growth is desirable [51]. The confirmation of guidelines for microbial $CO_2$ decrease at the cathode has been explored with a graphite stick cathode utilizing *Sporomusa ovata* as biocatalyst in this niche [52]. The planar graphite block as a cathode in MES couldn't accomplish high acetic acid derivation creation because of its restricted surface region for biofilm improvement. Various MES cathodes produced using carbonaceous, metallic, and carbon-metallic materials have been, as of late created, in MES. These materials can come in various setups including planar (like fabric, plate, and bar) and permeable 3D design (like froth and felt).

Permeable 3D materials with a huge specific surface area can upgrade microbial-anode cooperation and substrate versatility inside the cathode even without surface adjustment [17]. Different setups, for example, move through and gas dispersion cathodes [2,53], are additionally helpful in improving $CO_2$ decrease rate in MES. To additionally improve the cathode-microbial collaborations, cathode surface

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adjustments have been utilized [17]. Adjustments in cathode surface are intended to upgrade the electrocatalytic action and microbial cell adherence to the cathode. For instance, alteration of the carbon material terminal with chitosan, an amino and hydroxyl-bunch rich polysaccharide, expanded the acetic acid derivation/creation rate by 7.6-fold [54]. Creation of acetic acid derivation from $CO_2$ decrease was helped because of $CO_2$ adsorption on the permeable chitosan, upgraded electron movement relating to the biocompatible cathode surface, and better collaboration between the positive charges on chitosan and the negative charges on the outside surface of microbes.

Furthermore, carbon nanomaterials have been generally utilized for the upgrade of conductivity, specific surface area, and biocompatibility of MES cathodes. Multiwalled carbon nanotube (MWCNT) covering on reticulated glassy carbon (RVC) was reportedly first used to efficiently give a high explicit surface area for bacterial development and the relating acetic acid derivation [55]. The high conductivity of the RVC-based cathodes actuated by MWCNTs additionally prompted $\sim 100\%$ electron recuperation in MES [17]. Adjusting the carbon-based cathode with rGO additionally improved the $CO_2$ decrease rates utilizing *S. ovata* [27], upgrading the acetic acid derivation arrangement by 11.8 times when contrasted with the unmodified carbon fabric cathode in MES. Moreover, metal-carbon complex cathodes have likewise been applied in MES for $CO_2$ reduction of nickel (Ni) nanowire [25,29], $Fe_2O_3$ [56], and $Fe_3O_4$ [57–59] have been explored to modify carbonaceous materials as MES cathodes and add to the upgraded $CO_2$ decrease rates in MES due to the improved electrocatalytic property of the cathode material.

A photocathode prepared with silicon-titanium oxide nanowires (Si-$TiO_2$ NWs) has reportedly facilitated $4.4 \pm 1.0$ times higher cell stacking of *S. ovata* cells in comparison to planar Si cathodes [4]. In regards to cathode surface adjustments, there is a need to design a superior cathode structure to address the mass exchange limitation in MES. Gas dispersion terminal (GDE) produced using initiated carbon and the polytetrafluoroethylene (PTFE) VITO-CoRE has been explored in this way in MES. The VITO-CoRE GDE gave a strong gas-fluid interface for $CO_2$ dissemination, which improved $CO_2$ mass exchange [53]. Similarly, a constrained move through an arrangement of carbon felt cathodes upgraded the production rates in MES by improving the mass exchange and terminal surface area [2,17,55]. Strikingly, three layers of nonadjusted carbon felt as they move through the cathode at $-0.85$ V versus SHE delivered the most noteworthy rate of acetic acid derivation creation at $371 \pm 5$ g $m^{-2}$ $d^{-1}$ [60]. This system likewise delivered longer chain natural builds, for example, *n*-butyrate and *n*-caproate at the rate of $160 \pm 29$ g $m^{-2}$ $d^{-1}$ and $46 \pm 1$ $g^{-2}$ $day^{-1}$.

In the most recent modification of cathode engineering to address $CO_2$ mass exchange restriction, direct $CO_2$ supply in dual layer permeable Ni hollow fiber (Ni-HF) layer cathode has been shown to enhance the bioelectrochemical $CO_2$ decrease in MES [29,37]. Practically 84% of the electrons are reported to be recuperated as methane by means of $CO_2$ conveyance through Ni-HFs, accomplishing recycling with multiple times higher $CO_2$ transformation proficiency contrasted with $CO_2$ sparging into MES electrolyte [37]. A subsequent report placing MWCNT

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on the outside of Ni-HF further affirmed the prevalence of direct $CO_2$ conveyance over chemolithoautotrophs on the cathode, with enormously upgraded $CO_2$ adsorption limit and diminished electron transfer opposition, which prompted higher acetic acid derivation from $CO_2$ utilizing *S. ovata* contrasted with the unmodified Ni-HF [29]. The immediate $CO_2$ conveyance through permeable fiber terminals provided high $CO_2$ accessibility at the MES cathode surface, which resulted in higher synthesis of methane and acetic acid from $CO_2$. $CO_2$ concentration and air pocket/pore sizes may vary with $CO_2$ usage and bacterial development in MES. The impact of $CO_2$ concentration, stream rate, and air pocket size on $CO_2$ fixation has been investigated in cylindrical microalgae-bioreactors, and the outcomes showed that higher $CO_2$ fixation actuated higher cell fixation and photosynthesis efficiency [61]. These authors likewise noticed higher bacterial development with more modest $CO_2$ bubble sizes going from 31 to 61 mm by utilizing more modest pore size (5–10 μm) spargers, which could be credited to the improved gas-fluid interfacial area by reducing the air pocket size and hence upgrading mass exchange [61]. The $CO_2$ bubble size could be additionally diminished utilizing permeable layer anodes with small pore sizes ($<1$ μm), which can prompt better $CO_2$ mass exchange. Not only were the $CO_2$ mass exchange and accessibility said to be enhanced, but also the nearby pH at the terminal surface could be changed by direct $CO_2$ conveyance through the permeable layer cathodes in MES [62].

Acetic acid synthesis in MES has been reportedly investigated with stepwise alterations in media pH between 6.7 and 3 and one of the major acetic acid syntheses was accounted for at a pH of 5.2 [63]. It is apparent that a marginally acidic environment, having pH 5–6, advances the creation of multicarbon VFAs and represses the methane phase at the cathode. Since $CO_2$ sparging into media has been shown to have the option to make marginally acidic pH, nonstop $CO_2$ sparging alongside bicarbonate in media could be a fantastic option for keeping up pH at 5–6 in MES. Thinking about this load of discoveries, the future improvements on cathode engineering in MES could zero in additionally on permeable film/membrane terminals for direct gas conveyance and small air pocket creation to accomplish high $CO_2$ concentrations, quick mass exchange, and somewhat acidic pH at the cathode surface.

## 4. Use of chemolithoautotrophs MES biocathodes for $CO_2$ reduction

Chemolithoautotrophs can utilize $H_2$, formate, sulfide, and decreased metal particles as electron contributors for $CO_2$ decrease through the Wood-Ljungdahl (WL) pathway, turn around carboxyl acid, and variations of the hydroxypropionate/hydroxybutyrate pathways. Decreased electron benefactors, particularly $H_2$, could be created through HER at the cathode surface when an adequate reductive potential is forced under electrochemical settings. In addition, microorganisms may take up electrons straightforwardly from the cathode. Direct take-up of electrons from the cathode has been accounted for certain types of methanogens [64] and sulfate decreasing microbes [65]. The archaellum of *Methanospirillum hungatei* has been demonstrated

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to be electrically conductive [66], which may work with the direct electron transfer from cathode to microorganisms. Accordingly, chemolithoautotrophs could effectively join the terminals for $CO_2$ decrease with the power input. Homoacetogens address a grouping of systematically different chemolithoautotrophs that can utilize $CO_2$ and $H_2$ (electron donor) for anaerobic-autotrophic development. A few types of homoacetogens from the classes *Sporomusa*, *Moorella*, and *Clostridium* have been examined for $CO_2$ decrease to multicarbon items in MES [66].

Other than unadulterated societies of homoacetogens, blended microbial networks are broadly utilized as biocatalysts in MES. In blended cultures, the collaborations among different microorganisms can bring about a final microbiome adjusted to the proposed cycle. The utilitarian shift towards the ideal cycle and the versatile idea of blended societies to the operational condition in the reactors utilize blended culture networks invaluable for MES applications [67,68].

MES are normally immunized by blending with culture inocula from anaerobic conditions [55], recently enhanced inocula from parent MESs [63], as well as specific cultivation of designated species from blended culture [69]. A collection of $CO_2$-reducing microscopic organisms from the phylum Firmicutes, for example, *Acetobacterium* spp., *Acetoanaerobium* spp., *Trichococcus* spp., and *Clostridium* spp., have been overwhelmingly enriched in blended culture MES biocathodes [70]. High rates of $CO_2$ decrease have been demonstrated at the biocathode of MES, where chain-extending organisms likewise became dynamic for the bioelectrochemical change of $CO_2$ to medium-chain VFA creation [18].

In recent improvement in MES research, inocula from hypersaline conditions utilizing saltwater pool residue and interface electrolyte have been tried for the enhancement of homoacetogens at the cathode [37]. Genome examination has uncovered novel halophilic homoacetogens for $CO_2$ fixation by means of the WL pathway [37]. The activity of MES systems under saline conditions may be beneficial for profoundly increasing electrolyte conductivity, such as in seawater, which can be utilized to decrease ohmic hindrance. Choosing strong and successful $CO_2$ diminishing systems from saline environments that are varied in microbial arrangement, like a salt marsh, mangrove, or remote ocean residue, could be valuable for MES concentrate in this direction.

## 5. $CO_2$ usage to make a variety of products using the MES systems

The utilization of $CO_2$ as raw material for the synthesis of diverse chemical compounds through MES systems has been practiced by several researchers globally [5,16,22,24,34,37,62,71–73]. All in all, the acetic acid derivation is the most well-known bioproduct created from $CO_2$ transformation in MES. Be that as it may, some other substances, for example, butyrate, oxo-butyrate, ethanol, and isopropanol have additionally been created as minor items [5,16,18,22,24,34,37,47–49,62,71–74]. Synthesis of ethanol from $CO_2$ has been explored via utilization of *S. ovata* unadulterated culture, leading to profoundly reductive reactions with an abundance of

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accessible hydrogen [75,76]. Microbial chain elongation could be subsequently started to deliver up to $C_4$–$C_8$ items in the presence of acetic acid derivation and ethanol. The creation of longer-chain unsaturated fats from acetic acid derivation needs ethanol as an electron benefactor, yet in MES, under the profoundly reductive condition of the cathode or hydrogen, it likewise fills in as an electron donor for chain elongation [77]. Ethanol could be delivered as an intermediate through the decrease of acetic acid derivation utilizing hydrogen, even as van Eerten-Jansen et al. were the first to reveal the chain stretching of acetic acid derivation to caproate ($C_6$), utilizing the cathode as the electron benefactor [78].

Acetic acid derivation and other VFAs created from $CO_2$ in MES could be the antecedent mixtures for the bioproduction of other crude synthetic compounds. The creation of butyrate ($0.16\,g\,L^{-1}\,d^{-1}$) as the principal item from $CO_2$ reduction has been accounted for in MES [62]. Butyrate production rate from $CO_2$ in MES increased to $0.21\,g\,L^{-1}\,d^{-1}$ as a result of microbial transformation [74]. Butyrate and caproate creation rates came to be as high as $160 \pm 29$ and $46 \pm 1\,g\,m^{-2}d^{-1}$, respectively, when the acetic acid derivation creation was just about as high as $370\,g\,m^{-2}d^{-1}$ in persistent mode utilizing constrained course through carbon felt cathode [60]. Various other VFAs and alcohols have been synthesized using MES and creation rates have been upgraded with enhancements in cathode material properties and design [29,37,40,51,74,79]. The results from these reports show that MES is an attractive way to deal with $H_2$ supplying in situ electrons for anode-driven chain lengthening measures at the cathode.

MES as a manufacturing stage becomes appealing with regards to a circular economy when the production can be set at a high rate, and the finished products can be enhanced to become exceptional and financially significant items. In $CO_2$ reduction by means of the Wood-Ljungdahl (WL) pathway, acetyl-CoA is a focal antecedent that may go through an additional metabolic change to create different product synthetics like ethanol, butyrate, lactate, 2,3-butanediol, and butanol under the appropriate conditions. Solventogenesis metabolism can be adopted into the MES cycle by changing operational conditions to create individual alcohols from VFAs [18]. Such a point of view presents the MES as the maker of preliminary mixtures like $H_2$, $CH_4$, and acetic acid derivation/short-chain unsaturated fats (SCFA), which can be additionally moved up to longer chain carboxylates, biofuels, bioplastics, polysaccharides, and protein with multistep bioconversions [5]. Alongside other SCFAs, butyrate and caproate have been used in MES for derivation of acetic acid [60]. In different methodologies of additional change of SCFAs, creation of polyhydroxyalkanoates and single-cell proteins (SCPs) is feasible.

## 6. MES energy consumption reduction via integration of renewable energy and a chain-elongation platform

The financial problems of bioelectrochemical $CO_2$ have decreased with reference to various items (formic corrosive, acidic corrosive, and oxalic corrosive) as far as cost adequacy, energy, and crude material expenses have as of late been broken down [1].

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Since acetic acid derivation is the fundamental result of current MES deigns, the conversation on monetary examination is centered for the most part around acetic acid creation. In synopsis, one MES stack having a cathode surface area of 45 $m^2$ and an acetate conversion rate of 10 g $m^{-2}$ $h^{-1}$ could reportedly lessen 3.94 tons of $CO_2$ emission and yield 5.37 tons of acetic acid every year. Considering the power cost of 406 EUR/ton of acidic materials created with 30% electrical productivity, the absolute power cost for one MES stack will be around 2180 EUR/year [1], which is near the cost of the yearly substitution of anodes and layer materials (50 EUR/$m^2$). It is advantageous to specify that the energy cost does exclude the energy-concentrated cycles for acidic materials extraction. To make MES cost effective, it is important to essentially bring down the energy requirement for MES activity.

As referenced in Table 14.1, microbial $CO_2$ decrease at the cathode could be accomplished by applying a low cathode potential of less than −0.4 V versus SHE. Likewise, competent OER surfaces or photograph/bio-enabled anodes could be used to drive productive electrons at the anode surface eliminating the

**Table 14.1** Membranes and energy input for low-cost production of volatile fatty acids (VFAs) synthesis through bioelectrochemical methods.

| Membrane/ material used | Input Energy for extraction[a] (kWh $kg^{-1}$) | Cathode | Synthesized compound | Citation |
|---|---|---|---|---|
| AEM | ∼30.5 | Graphite felt | Acetate | [80] |
| AEM | 2 | 316 L SS | $C_2$–$C_6$ | [72] |
| AEM & CEM | 5.43 | Ti mesh | Acetate, butyrate propionate | [81] |
| 10 AEM & CEM | 0.395 | Pt coated Ti plate | VFAs | [73] |
| AEM | 2 | SS felt | Caproic acid | [82] |
| AEM | 4.08 ± 0.66 | SS mesh | *n*-Caproic/ caprylic acid | [83] |
| 10 bipolar 10 AEM 1 CEM | 6.3 | 316 SS | Succinic acid | [84] |
| CEM & AEM | 26.5 | Carbon felt | Acetate | [24] |
| Bipolar membrane (BPM) | 30.7 | | Acetate | |
| Cation exchange membrane (CEM) | 44.3 | | Acetate | |
| CEM and anion exchange membrane (AEM) | 19 | Carbon felt | Acetate | [85] |

[a]*Computed as per the energy consumption $kg^{-1}$ of the product synthesized from the bioreactors.*

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requirement of additional energy for carrying out the concerned process. Aside from these strategies for decreasing energy utilization for MES activity, using renewable energy to supplant the conventional power supply could be another choice for future MES increase and support other combinations [54]. The expanding plenitude and decreased expense of inexhaustible power for sun-oriented MES is approaching equality with petroleum products, making $CO_2$ change through MES increasingly attractive when fueled by sustainable power sources. As the hypothetical energy contribution for one ton of acetic acid synthesis would reach 4.06 MWh with 30% energy proficiency [1] , the all-out energy cost would be the US $162.4–243.6 on the off chance that we power MES with sun-based power. This represents a huge reduction from the current MES energy cost (406 EUR/ton) for acetic acid synthesis, as referenced above, and an incredible overall revenue compared to the current market cost of acetic acid, which is ∼US$625/ton acidic corrosive [79].

Sustainable power from photovoltaic (PV) boards is a novel innovation to reap sun-based energy for meeting the requirements of a MES setup. Sun-powered material efficiency of 10% could be accomplished given the expectation of 20% sunlight based on electrical change productivity utilizing an industrially accessible PV board with electrical-to-material effectiveness of 52% [86]. Aside from PV boards, photoelectrodes could be applied in MES to additional improve sun-based harvesting productivity. A microbial PEC system outfitted with dark silicon photocathode and bioanodes for hydrogen synthesis has been created with exclusively sunlight-based energy as a power source, accomplishing a 93%–97% electron recuperation as hydrogen [87]. To additionally upgrade the sunlight-based energy harvesting effectiveness, semiconductors with a tight bandgap ought to be created to empower higher light assimilation [26].

Notwithstanding the energy contribution for MES activity, the energy utilization and the material expenses depend on higher energy for acetic acid synthesis, regardless of whether environmentally friendly power is utilized to control MES or not. In conventional processes, most of the acetic acid is separated or purged through distillation, azeotropic refining, and fluid extraction, which normally are energy intensive and require complex infrastructure [88]. Nonetheless, because of the idea of MES systems, the media or overflowing contains a lot of salts and suspended biomass, which could be possibly separated together with acetic acid and sully the filtration measures. Film innovation is in this way presented for VFA partition, just as bacterial control in food and biotechnology ventures. Film electrolysis [83] or else membrane liquid-liquid [89] extraction have been used for in situ extraction of VFAs from anaerobic maturation and MES. VFAs with various carbon-chain lengths have been effectively extricated from the aging stock, utilizing ion-exchange membranes or polymeric hollow fiber membrane modules [89]. Almost 100% extraction of matured acetic acid by layer electrolysis has been attained with a maximum acetic concentration of 80 mM, demonstrating the potential of film electrolysis in MES application [71].

Extraction productivity of over 94% with acetic acid focus as high as 220 mM seemed to have been accomplished by planning a three-chamber MES reactor and

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coordinating an anion exchange membrane (AEM) and a cation exchange membrane (CEM) for membrane electrolysis [85]. Be that as it may, the increasing saltiness of the extraction fluid and the potential fouling of AEM for film electrolysis may prompt decreased extraction effectiveness for MES activity. Another extraction strategy using ion-exchange resin for acetate sorption from MES stock has likewise been applied [2]. Acetate adsorption sorption of 10–20 $mg\,g^{-1}$ resin has been observed in the wake of recycling the catholyte through the ion-exchange resin. The extraction productivity was lower contrasted with layer electrolysis, likely because of the great partiality among water and acetic acid derivation atoms, the salt amassing, and biofouling.

To lessen the energy cost for extraction and make MES more feasible for modern $CO_2$ reduction, it is necessary to convert the acetic acid synthesized over to medium-chain carboxylic acids, which have higher market cost, for example, caproic acid ($1.6/kg) [71] and butyric acid (>$3.5/kg) [16,35], and lower water solvency than acetic acid derivation. Extraction of medium-chain unsaturated fats (MCFAs) is preferable since it requires substantially less energy input (<2 $kWh/m^3$) compared to acetic acid synthesis/extraction (Table 14.1). After the microfiltration of MES effluent, chain elongation from acetate might be done in MES reactors or in separate fermentation reactors. A membrane liquid-liquid extraction unit using hollow fiber membranes prepared with 6% dodecanol has been used to extract butyrate from an MES reactor as per literature [74]. Within the MES reactor, acetate can be chain elongated to butyrate, with ethanol serving as electron donors. The high selectivity of butyrate (16.4) over acetate demonstrates the potential for chain-elongation technology in MES to minimize the energy cost of VFA extraction [74].

For the separation of medium-chain carboxylic acids after chain elongation using membrane electrolysis, minimum power consumption of 4.08 0.66 $kW\,h\,kg^{-1}$ product extracted has been attained, which is significantly less than the energy input for acetate extraction using the same technique [83]. Khor et al. used membrane electrolysis in a fermentation system for the electricity-assisted generation of caproic acid from grass to reduce the energy consumption for caproic acid extraction (2 $kWh\,kg^{-1}$ carboxylic acid extracted) [82], showing a significant reduction in energy usage for bioproduct extraction. As a result, an MES-based production and extraction system would be useful in promoting the circular bioeconomy. MES could serve as a supplementary technology to AD in the future if it fully utilizes its anode compartment for wastewater treatment and boosts its profitability, even though the caproate production rate in MES is still slower than that in AD due to chain elongation.

## 7. Future perspectives

Change from the model of material and energy consumption to a circular bioeconomy is a vital angle in management of natural resources for ensuring a sustainable future. The MES stage could include the utilization of inexhaustible power for

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$CO_2$ reuse and byproduct creation, showing a promising possibility for power-driven bioproduction of short and MCFAs from $CO_2$ utilizing acetogenic microbes as biocatalysts. MES can additionally assume a corresponding part in accomplishing a circular $CO_2$/bio-based economy, in the event that we can defeat some restricting elements to its application, for example, high working costs and low item specificity.

The $CO_2$ con-adaptation rates must be significantly enhanced to bring MES to the level of mechanical application, which could be accomplished through the advancement of chemolithoautotrophs aided by ensuring appropriate $CO_2$ availability and electron donors. $CO_2$ conveyance to biofilm has been demonstrated to be successful using improved permeable layer cathodes and gas dissemination anodes in MES frameworks [90,91,95]. Higher $CO_2$ concentrations and smaller $CO_2$ bubbles have been shown to result in a higher mass exchange coefficient, which increased $CO_2$ utilization and bacterial development [53,92–94]. As a result, gas dissemination anodes and electrically conductive and synergist-permeable layers could be used to bring MES technology towards commercialization. However, a few activity conditions, such as vaporous $CO_2$ stream rates, bubble size, and gas dissemination at the cathode-organism media interface, which are known to significantly improve MES execution, should be streamlined prior to attempting to convert this type of cathode engineering into a large-scale modern application.

To nurture better strategies for upgrading VFA production rates from $CO_2$ decrease, better downplaying of electron transport components from the cathode to chemolithoautotrophs is required. Direct electron transport (DET) from the anode to chemolithoautotrophs appears to be thermodynamically superior to backhanded electron transport via electrochemically generated hydrogen. In any event, in mixed culture biocathodes, the combination of both electron transport mechanisms is extremely likely. As a result, a clear understanding of the dominant system in MES (i.e., direct versus $H_2$-interceded electron transport) is critical for a sound cathode design. For example, if immediate electron transport is the primary mode of operation, biocompatible cathodes with a large specific surface area are required for bacterial connection, whereas for $H_2$-interceded electron transport, the cathode configuration can be changed by presenting more dynamic destinations for improved HER.

The identification of extremely productive chemolithoautotrophs is critical. One viable option could be the hereditary creation of suitable species. The acetogen *Clostridium ljungdahlii*, for example, was biologically optimized to produce more significant bio-items (such as butyrate) from $H_2$:$CO_2$ [18]. Microorganisms found in saline living environments such as mangroves and salt marshes provide ideal conditions for $CO_2$ fixing species and play an important role in the carbon cycle. As a result, saline environments may become a good place for discovering unique and effective $CO_2$ fixing networks that might potentially produce useful matter with a wide digestive range.

At present, another challenge for boosting MES may be the energy cost of MES activities. To reduce energy input, several procedures could be used, such as combining environmentally friendly power sources with MES, decreasing anodic OER

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with minimal expense and effective impetus, using saline electrolyte to reduce ohmic loss, and chain extension of short-chain fatty acids (SCFA) to MCFAs for simple extraction. To foster MCFA creation measures with high productivity, dependability, and controllability, more research into power-driven microbial chain prolongation is required. Nonetheless, a complete energy analysis should be conducted to determine how much energy is used by the various sections of the MES.

Future advancements in MES from $CO_2$ include the use of cross-breed systems such as autotrophs for $CO_2$ reduction and heterotrophs for extra item modification following $CO_2$ reduction. Similarly, autotrophic-heterotrophic mixtures and heterotrophic-heterotrophic mixtures may be applied simultaneously (as biocathode and bioanode, respectively) for treatment of natural waste streams in an energy efficient manner. Combining MES with well-established biotechnologies such as AD and maturation is a viable alternative for future applications.

## 8. Conclusion

The challenges accompanying new MES stages for the blend of bioproducts from $CO_2$ are summarized in this discussion. To reduce energy consumption, detailed strategies for productive anodic electron aging and bioproduct extraction have been developed. MES cathodes with direct $CO_2$ conveyance and incredibly productive chemolithoautotrophy have been reportedly established to increase bioproduct development, in addition to the usual requirements of high surface area and strong bacterial bond. In the case of collaborative development with environmentally friendly electricity, wastewater treatment, anaerobic digestion, and aging, the use of MES frameworks is advocated so that a circular bioeconomy of $CO_2$ reduction and various compound syntheses may be achieved.

Seed culture, pH, temperature, nutrients availability, hydraulic retention time, hydrogen partial pressure, fermentation end-products, polarization losses, activation losses, concentration polarization, ohmic losses, microbial interaction with the electrode surface, and $O_2$ reduction by the cathode are all factors that influence MES-mediated energy/product generation in the context of bioelectricity as well as biohydrogen from wastewater as a potential substrate. It is a reality that relatively few studies have been undertaken on these parameters, and more study is needed to address these difficulties in order to improve overall process efficiency and make BES-mediated waste valorization an economically viable and practicable method.

## Declaration of competing interest

The authors declare that there is no competing interest whatsoever. All authors have contributed equally to the writing of this chapter.

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# Index

Note: Page numbers followed by *f* indicate figures and *t* indicate tables.


## A

Acetic acid synthesis, 264
Activated sludge method, 246–247
Aerobic treatment, 246
Agricultural wastewater treatment, 230
Algae, 243
Algae-based microbial fuel cell (MFC), 2–3
  algal biofilm bioreactors, 8
  bioelectricity generation, 4–6
  carbon dioxide, 22–23
  construction of, 18–20, 19*f*
  current status, 11
  dissolved oxygen, 22–23
  electricity generation, 18–20
    anode, 19–20, 20*t*
    cathode, 18, 19*t*
  electrodes, 22
  end-product in, 23–24
  future perspectives, 11
  light intensity, 22, 23*f*
  limitations, 24
  membrane, 22
  operational parameters of, 4–6
  oxidation and reduction reactions (ORR), 4–5
  pH, 21
  photosynthetic algal microbial fuel cells (PAMFCs), 3
  prospects, 24
  reactor, 6–7
  role of, 4
  sediment microbial fuel cells (SMFC), 3
  Stefan-Boltzmann law, 5
  substrate, 21–22
  temperature, 21
  value-added products recovery, 10, 10*t*
Algal biofilm bioreactors, 8
Anaerobic treatment, 247
Animal farming wastewater treatment, 230–231
Anion exchange membrane (AEM), 160–161, 268–269
Anode, 19–20, 20*t*, 154–156
  associated materials, 155
  carbon anode, carbonaceous material to, 155–156
  carbon-based anodes, 154
  carbon cloth, 155
  carbon nanotubes, 156
  graphite, 155
  meshes, 155
  metal-based/noncarbon anodes, 156
  paper, 155
  respiring bacteria, 103
Anode modification
  electrodes, 135–137
    biocompatibility, 137
    cost and accessibility, 136
    electric conductivity, 136
    environmentally friendly, 137
    properties, 135–137
    stability and durability, 136
    surface area and porosity, 136
  microbial fuel cell (MFC), 134–135, 135*f*, 137–146, 139–141*t*
    carbon anode, 138–143, 142*f*
    chemical anodic modifiers, 145–146
    conductive polymer for, 144–145
    metal oxide nanocomposites, 146
    nickel anode, 143–144
    Pt anode, 143
Atomic layer deposition (ALD), 261

## B

Bacteria, 241
Bioaccumulation technique, 72
Bio-based membranes, 194
Bioelectricity generation, 4–6
Bioelectrochemical systems (BES)
  applications of, 87–91
    ethanol, 89
    hydrogen peroxide, 89
    methane, 89
    product formation, 88
    product recovery, 88
    recalcitrant pollutant degradation, 90–91
    recovery of nutrients, 87
    valorizing carbon dioxide, 87–88
    valorizing contaminated water, 88
    valorizing energy, 88




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Bioelectrochemical systems (BES) *(Continued)*
classification, 80–84
electron transfer, 85–87
extracellular, 85–86
intracellular, 86–87
enzymatic ES, 83–84
enzyme-mediated electrochemical system, 126
factors affecting, 91–93
different substrate effect, 91–92
electrode effect, 91
external resistance effect, 93
pH effect, 92
reactor type effect, 92
temperature effect, 92–93
future prospects, 94, 129
greenhouse gases (GHGs), 80
mechanism, 122–124
anodic mechanism, 122–123
cathodic mechanism, 123–124
membrane-integrated bioelectrochemical system (MIBES), 51–59
membranes. (*see* Membranes)
microbial electrochemical system, 124–125
microbial ES, 82–83
necessity, 84
principle, 81–82
proton-exchange membrane fuel cells (PEMFCs), 80
shortcomings of, 93
thermodynamics, 81–82
transfer of electron in, 126–128
extracellular transfer of electrons, 126–127, 127*f*
interspecies, 127–128
intracellular, 128
types of, 124–126
wastewater treatment
applications in, 128–129
high and low biodegradable component, 128–129
integrated processes for, 129
working of, 84
Biological oxygen demand (BOD), 243
Bioremediation, 72
Biosorption, 72
Bipolar membranes (BPMs), 161
Brewery/distillery wastewater treatment, 229

## C

Carbon anode, 138–143, 142*f*
Carbon dioxide, 22–23
Carbon fiber brush cathode (CFBC), 7
Cathode, 18, 19*t*, 106, 156–158
abiotic cathodes, 157
biotic cathodes, 157–158
cathode catalyst, 158, 159*t*
Cation exchange membrane (CEM), 160, 268–269
Cell density, 4
Cementation, 71–72
Ceramic-based membranes, 193–194
Ceramic-based separator, 161
Chemical anodic modifiers, 145–146
Chemical oxygen demand (COD), 243, 261
Chemical precipitation, 70–71
Chemolithoautotrophs, 264–265
*Chlorella vulgaris*, 3
Chlorine evolution reaction (ClER), 260–261
Chlorophyll, 4
Conductivity, 178
CRISPR/Cas9, 250
Cyanobacteria, 4
Cyanobacteria-based microbial fuel cells
advantages of, 106, 111–112
alternative energies, 99–102
biofuels, types of, 100–101
microalgae, 101–102
anode, 106
basic structure of, 103–104, 103*f*
cathode, 106
challenges associate with, 109–111
activation losses, 110
concentration losses, 111
Ohmic losses, 110–111
components of, 104–106
electrode materials, 105
future perspectives of, 113–114
mediators, 105
membranes, 105–106
microbial fuel cell (MFC), 102–106
water pollution and waste management, 106–109
leachate treatment, 109
wastewater treatment, 107–108

## D

Different substrate effect, 91–92
Dissolved oxygen, 22–23
Diversity of microbes, 38
algae, 38
bacteria, 37
fungi, 38
helminths, 39
protozoa, 37–38
virus, 39
Domestic/municipal wastewater treatment, 229
Double-chambered MFCs, 162–163, 163*f*
Dynamic membrane (DM), 52

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## E

Electricity generation, 18–20
  anode, 19–20, 20*t*
  cathode, 18, 19*t*
Electrochemical oxidation (EO), 122–123
Electrode effect, 91
Electrode materials, 105
  anode, 154–156
    associated materials, 155
    carbon anode, carbonaceous material to, 155–156
    carbon-based anodes, 154
    carbon cloth, 155
    carbon nanotubes, 156
    graphite, 155
    meshes, 155
    metal-based/noncarbon anodes, 156
    paper, 155
  cathode, 156–158
    abiotic cathodes, 157
    biotic cathodes, 157–158
    cathode catalyst, 158, 159*t*
Electrodes, 22, 135–137
  biocompatibility, 137
  cost and accessibility, 136
  electric conductivity, 136
  environmentally friendly, 137
  properties, 135–137
  stability and durability, 136
  surface area and porosity, 136
Electron transfer, 85–87
  extracellular, 85–86
  intracellular, 86–87
Eletricigens, 103
Energy consumption
  recovery, 207–209
  reduction, 266–269, 267*t*
Enzymatic ES, 83–84
Ethanol, 89
Exoeletricigens, 103
External resistance effect, 93, 176–177

## F

Fluorescent in situ hybridization, 249
Fluorine-doped tin oxide (FTO), 261
Food and beverage industry, 41
Forward osmosis (FO), 53, 68
Fossil fuels, 100
Fungi, 243–244

## G

Gas dispersion terminal (GDE), 263
Gas permeable (GP) membrane, 53
Genetically modified microorganism (GMO), 248–249
Greenhouse gases (GHGs), 80

## H

Hybrid BESs integrated with membrane based technologies, 201–206
  microbial desalination cells, 201–202
  microbial reverse-electro dialysis cells, 203–204
  osmotic microbial fuel cells, 202–203
  pressurized filtration-microbial fuel cells, 204–206, 205–207*t*
Hydrogen peroxide, 89
Hydropower, 99–100

## I

Industrial wastewater treatment, 222–226*t*
  bioelectrochemical systems, 227–233, 227–228*f*
    agricultural wastewater treatment, 230
    animal farming wastewater treatment, 230–231
    brewery/distillery wastewater treatment, 229
    domestic or municipal wastewater treatment, 229
    landfill leachate treatment, 231
    microbial fuel cells (MFCs), 220
    palm mill oil effluent treatment, 231
    paper and pulp industry wastewater treatment, 232
    petroleum wastewater treatment, 232
    pharmaceutical wastewater treatment, 232–233
  configuration, 221–227
  future perspectives, 233
  operational mechanism, 221–227
Inoculum
  exoelectrogens isolated from, 169
  mixed cultures used as, 169–171, 172*t*
  pure cultures used as, 167–169, 170*t*
Ion exchange membranes (IEMs), 160–162
  anion exchange membrane (AEM), 160–161
  bipolar membranes (BPMs), 161
  cation exchange membrane (CEM), 160
  ceramic-based separator, 161
  salt bridge, 162
  size-selective separators, 161

## L

Landfill leachate treatment, 231
Leachate treatment, 109
Light intensity, 22, 23*f*


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## M

Mediators, 105
Medium-chain unsaturated fats (MCFAs), 269
Melanin nanoparticles impregnated membranes, 196–200, 197–200*t*
Membrane-integrated bioelectrochemical system (MIBES)
  advantages, 59
  bioelectrochemical system (BES), 50–51
  challenges associated with, 58
  classification of, 53–58
  disadvantages, 59
  dynamic membrane (DM), 52
  forward osmosis (FO) membrane, 53
  future perspectives, 59
  gas permeable (GP) membrane, 53
  membranes, types of, 51–53
  microbial desalination cell, 57–58, 57*f*
  microbial fuel cell (MFC), 53–55, 54*f*
  microbial reverse electro-dialysis cell, 55–57, 56*f*
  ultrafiltration (UF) membrane, 52
Membranes, 105–106
  bio-based membranes, 194
  ceramic-based membranes, 193–194
  current challenges, 209–211
  energy consumption and recovery, 207–209
  future perspectives, 209–211
  hybrid BESs integrated with membrane based technologies, 201–206
    microbial desalination cells, 201–202
    microbial reverse-electro dialysis cells, 203–204
    osmotic microbial fuel cells, 202–203
    pressurized filtration-microbial fuel cells, 204–206, 205–207*t*
  impregnation of nanomaterials onto, 194–200
    melanin nanoparticles impregnated membranes, 196–200, 197–200*t*
    metal nanomaterials impregnated membranes, 194–195
    semiconductor nanoparticles impregnated membranes, 195–196
  polymer-based membranes, 192–193
  types of, 192–194
Metal nanomaterials impregnated membranes, 194–195
Metal oxide nanocomposites, 146
Metazoa, 242–243
Methane, 89
Methanogenesis, 175
Microalgae-based bioelectrochemical system, 2
Microbes, 247
  microbial electrical remediation technology, 250–251
  rDNA technology, 248–250
    biodegradation rates, 249–250
    CRISPR/Cas9, 250
    fluorescent in situ hybridization, 249
    polymorphic DNA, random amplification of, 249
  16S rRNA, 247–248
  wastewater, characteristics of, 244–245
    activated sludge method, 246–247
    aerobic treatment, 246
    anaerobic treatment, 247
    methodologies used for, 243–244
    primary treatment, 246
    secondary treatment, 246–247
    tertiary treatment, 247
    trickling filters, 247
  wastewater treatment, diversity in, 240–244, 240*f*
    algae, 243
    bacteria, 241
    fungi, 243–244
    metazoa, 242–243
    protozoa, 241–242, 242*t*
Microbial carbon capture cell (MCC), 9–10
Microbial desalination cell (MDC), 50–51, 57–58, 57*f*
Microbial desalination cells, 201–202
Microbial electrical remediation technology, 250–251
Microbial electrolysis cell (MEC), 50–51
Microbial-electro remediation technique, 49–50
Microbial electrosynthesis (MES), 1–2
  acetic acid synthesis, 264
  anion exchange membrane (AEM), 268–269
  atomic layer deposition (ALD), 261
  cation exchange membrane (CEM), 268–269
  chemical manufacture, 262–264
  chemical oxygen demand (COD), 261
  chemolithoautotrophs, 264–265
  chlorine evolution reaction (ClER), 260–261
  $CO_2$
    products variety, 265–266
    reduction, biocathodes for, 264–265
  efficient electron generation, anode tuning for, 259–262
  energy consumption reduction, 266–269, 267*t*
  fluorine-doped tin oxide (FTO), 261
  future perspectives, 269–271
  gas dispersion terminal (GDE), 263

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medium-chain unsaturated fats (MCFAs), 269
multiwalled carbon nanotube (MWCNT), 263
reduced graphene oxide (rGO), 260–261
reticulated glassy carbon (RVC), 263
sulfide oxidizing bacteria (SOB), 262
volatile fatty acids (VFAs), 258–259
Microbial electrosynthesis cells (MECs), 50–51, 82–83, 124
Microbial fuel cells (MFC), 50–51, 53–55, 54*f*, 102–106
biological factors, 166–176
inoculum, type of, 166–171
substrate in anodic chamber, 171–175
chemical and operational factors, 176–178
conductivity, 178
external resistance, 176–177
ionic strength, 178
organic loading rate (OLR), 177
pH, 177–178
substrate type, 176
temperature, 178
electrodes, 137–146, 139–141*t*
carbon anode, 138–143, 142*f*
chemical anodic modifiers, 145–146
conductive polymer for, 144–145
metal oxide nanocomposites, 146
nickel anode, 143–144
Pt anode, 143
future prospects, 179
methanogenesis in, 175
operation, start-up time for, 176
physical parameters, 154–165
double-chambered MFCs, 162–163, 163*f*
electrode material. (*see* Electrode material)
ion exchange membranes (IEMs), 160–162
reactor arrangement, 162–165
reactor components, 154–165
separators in, 158–162
single-chambered MFCs, 163–164, 164*f*
stacked MFCs, 164–165, 165*f*
upflow MFCs, 165, 166*f*
Microbial reverse-electro dialysis cells, 55–57, 56*f*, 203–204
Microorganisms in industrial wastewater treatment
diversity of microbes, 38
algae, 38
bacteria, 37
fungi, 38
helminths, 39
protozoa, 37–38
virus, 39
food and beverage industry, 41
nutrients, 33
oil spills, 36
oxygen, 34
paper and pulp industry, 39–40
pesticides/organic chemical pollutants, 35
pharmaceutical industry, 42–43, 42*t*
pharmaceuticals and personal care products (PPCPs), 34
sediments, 35
suspended solids, 35
temperature, 36
textile industry, 40–41
water pollution, sources of, 33–37
Molecular weight cutoff (MWCO), 66–67
Multiwalled carbon nanotube (MWCNT), 263

## N

Nanowires, 126–127
Nickel anode, 143–144
Nitrogen gas, 7
Novel functional materials, 64
Nutrients, 33

## O

Oil spills, 36
Organic compounds, 244
Organic loading rate (OLR), 177
Organic volatile compounds, 246
Osmotic microbial fuel cells, 202–203
Oxidation and reduction reactions (ORR), 4–5
Oxidation/reduction reactions, 72
Oxidoreductases, 126
Oxygen, 4, 34

## P

Palm mill oil effluent treatment, 231
Paper and pulp industry wastewater treatment, 39–40, 232
Pesticides/organic chemical pollutants, 35
Petroleum wastewater treatment, 232
PH, 21, 177–178
Pharmaceutical industry, 42–43, 42*t*
Pharmaceuticals and personal care products (PPCPs), 34
Pharmaceutical wastewater treatment, 232–233
pH effect, 92
Phosphate buffer solution (PBS), 7
Photosynthetic algal microbial fuel cells (PAMFCs), 3
Plain carbon paper cathode (PCPC), 7
Polyaromatic hydrocarbons (PAH), 243–244

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Polymerase chain reaction (PCR) amplification, 247–248
Polymer-based membranes, 192–193
Polymorphic DNA, random amplification of, 249
Power density (PD), 104
Pressurized filtration-microbial fuel cells, 204–206, 205–207*t*
Primary treatment, 246
Product formation, 88
Product recovery, 88
Proton exchange membrane (PEM), 6
Proton-exchange membrane fuel cells (PEMFCs), 80
Protozoa, 241–242, 242*t*
Pt anode, 143

## R

rDNA technology, 248–250
  biodegradation rates, 249–250
  CRISPR/Cas9, 250
  fluorescent in situ hybridization, 249
  polymorphic DNA, random amplification of, 249
Reactor arrangement, 162–165
Reactor components, 154–165
Reactor type effect, 92
Recalcitrant pollutant degradation, 90–91
  dye removal, 90
  leachate treatment, 90–91
  organochlorine removal, 91
  sulfide removal, 90
Recovery of nutrients, 87
Reduced graphene oxide (rGO), 260–261
Reticulated glassy carbon (RVC), 263
Reuse of treated wastewater
  advanced oxidation processes (AOPs), 62–63
    adsorption, 63–64
      polymer nanocomposites for, 64, 64*f*
    disadvantages of, 63
    photocatalysis, 62–63, 63*t*
  advance technologies for, 62–72
  anaerobic digestion (AD) process, 69–70
  biological wastewater treatment technology, 69–70
  contaminated water, metalloids remediation in, 70–72
  desalination technology, 70
  heavy metals nanotechnologies, 70–72
  membrane filtration technologies (MFT), 65–68, 66*t*, 67*f*
    microfiltration (MF), 66
    nanofiltration (NF), 68
    reverse osmosis (RO), 68, 69*t*
    ultrafiltration (UF), 66–67
  ozonation, 64–65
  soil aquifer treatment (SAT), 61
  water security, water-energy Nexus for, 73
Reverse osmosis (RO), 73

## S

Salt bridge, 162
Secondary treatment, 246–247
Sediment microbial fuel cells (SMFC), 3
Sediments, 35
Semiconductor nanoparticles impregnated membranes, 195–196
Single-chambered MFCs, 163–164, 164*f*
Size-selective separators, 161
Sodium sulfate, 4
Stacked MFCs, 164–165, 165*f*
Stefan-Boltzmann law, 5
Substrate, 21–22
  anodic chamber, concentration of substrate, 175
  type of, 172–174, 174*t*, 176
Sulfide oxidizing bacteria (SOB), 262
Suspended solids, 35

## T

Temperature, 21, 36, 178
Temperature effect, 92–93
Tertiary treatment, 247
Textile industry, 40–41
Thermodynamics, 81–82
Transfer of electrons, 50–51
Transmembrane pressure (TMP), 66
Trickling filters, 247

## U

Ultrafiltration (UF) membrane, 52
Upflow MFCs, 165, 166*f*

## V

Valorizing
  carbon dioxide, 87–88
  contaminated water, 88
  energy, 88
Value-added products recovery, 10, 10*t*
Volatile fatty acids (VFAs), 258–259

## W

Wastewater treatment
  characteristics of, 244–245
    activated sludge method, 246–247
    aerobic treatment, 246

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anaerobic treatment, 247
methodologies used for, 243–244
primary treatment, 246
secondary treatment, 246–247
tertiary treatment, 247
diversity in, 240–244, 240*f*
algae, 243
bacteria, 241
fungi, 243–244
metazoa, 242–243
protozoa, 241–242, 242*t*
Water pollution, sources of, 33–37

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