Advances in Environmental Electrochemistry

Edited by
Dipak Ashok Jadhav
Manaswini Behera
Surajbhan Sevda
Maulin P. Shah

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Biography

Dr. Dipak Ashok Jadhav

Dr. Dipak is an Assistant Professor of the School of Civil Engineering and Environmental Sciences in the JSPM University, Pune, Maharashtra, India. He did Ph.D. from the School of Water Resource, Indian Institute of Technology (IIT) Kharagpur on the development of scalable microbial fuel cell (bioelectric toilet) for sanitation applications. Earlier, he was associated as a Research Professor at the Department of Environmental Engineering at Korea Maritime and Ocean University, Busan, South Korea. Dr. Dipak has 6 years of post-Ph.D. experience including academic and research positions. Earlier, he was worked as an Assistant Professor, Maharashtra Institute of Technology, Aurangabad, India. During his MTech, he received DAAD fellowship to work in Technical University Braunschweig, Germany.

Dr. Jadhav has received several prestigious awards and fellowships including Young Technological Innovation Award (GYTI) at Rashtrapati Bhavan, IEI-Promising/Young Engineers Award, Brain Pool Fellowship, Swachhta Saarthi Fellowship, DAAD-IGCS Fellowship, Silver Medal for postgraduate studies at IIT Kharagpur, and many more. His research area includes microbial fuel/electrolysis cell, bioelectrochemical system, environmental electrochemistry for bioenergy, bioelectrosynthesis, and waste-to-resource recovery. Field demonstration of bioelectric toilet concept was appreciated by Ministry, Government of India with Swachthon 1.0 Award in 2018. To his credits, there are about 65 papers in various peer-reviewed *SCI* journals of high-impact factors (cumulative IF-450 with a paper of IF-36; citation $\sim$2500; h-index: 26) and also authored 25 book chapters and 6 ongoing edited books. He has presented the research work at national and international conferences (30+) in the area of bioelectrochemical system and bioenergy. He delivered keynote lectures in IITs, NITs, and foreign universities related to waste-to-resource recovery. Dr. Jadhav is also serving as an associate editor, editorial board member/reviewers for many international journals, and member of several scientific societies in the field of microbial fuel cell, microbial electrochemical system, and bioenergy research.

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Dr. Manaswini Behera

Dr. Manaswini Behera is an Associate Professor of Environmental Engineering in the School of Infrastructure, Indian Institute of Technology Bhubaneswar, India. She has received her Ph.D. in Environmental Engineering from the Indian Institute of Technology Kharagpur and Master's degree in Environmental Engineering and Management from the Indian Institute of Technology Delhi. She has joined IIT Bhubaneswar in 2014. Prior to joining IIT Bhubaneswar, Dr. Manaswini was associated with Veer Surendra Sai University of Technology, India, and National Institute of Technology Rourkela, India.

Dr. Manaswini has contributed 43 research papers in the journals of international repute and contributed 30 book chapters. Her research work has been presented in more than 37 conferences in India and abroad. She has guided 8 Ph.D. research scholars and 20 master students' projects. She has been working in the field of anaerobic wastewater treatment, bioenergy recovery during wastewater treatment using microbial fuel cell, and bio-electrochemical systems. Her area of research also includes ceramic separator development for microbial fuel cell, grey water treatment and reuse, nitrogen removal through anammox process, and emerging contaminant removal. She has successfully completed many sponsored research projects. At present, she is the investigator for the ongoing multinational collaborative project, SARASWATI-2.0 jointly funded by the European Union and Department of Science and Technology, Government of India, on best available alternative technologies for decentralized wastewater treatment and resource recovery in India. She has got a patent on using ceramic separator as a cost-effective alternative to expensive polymeric membrane in microbial fuel cell. She is currently serving as the associate editor of the *ASCE Journal of Hazardous, Toxic, and Radioactive Waste*. She has received recognition of her research contribution by getting elected as Life Member, Indian Water Works Association; Member, Institution of Engineers, India; Member, ASCE; Odisha Young Scientist Award in the category of Engineering and Technology, 2019, by Science and Technology Department, Government of Odisha; best paper awards at several conferences such as RECYCLE 2018, CESE 2018, ICONSWM 2019, ICBSEE 2022, ISSWM 2023, and Springer best paper award at ICPCCE 2023.

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Dr. Surajbhan Sevda

Dr. Surajbhan Sevda completed Doctoral Degree in 2013 from the Indian Institute of Technology Delhi, New Delhi, India. He is currently working as an Assistant Professor at the Department of Biotechnology, National Institute of Technology Warangal, India. Prior to this, he was a technical officer (research scientist) at IIT Guwahati, India. He has published more than 40 articles in scientific journals and 32 book chapters. His research experience lies in industrial wastewater treatment, biofuels, and bioenergy, life cycle analysis, metal recovery, biosensor development, green chemistry, and microbial electrosynthesis.

Dr. Maulin P. Shah

Maulin P. Shah is currently working as a Deputy General Manager—Industrial Wastewater Research Lab, Division of Applied and Environmental Microbiology Lab at Enviro Technology Ltd., Ankleshwar, Gujarat, India. He received his Ph.D. (2002–2005) in Environmental Microbiology from Sardar Patel University, Vallabh Vidyanagar, Gujarat. He has served as an Assistant Professor at Godhra, Gujarat University, in 2001. He is a Microbial Biotechnologist with diverse research interest. A group of research scholars is working under his guidance on the areas ranging from applied microbiology, environmental biotechnology, bioremediation, and industrial liquid waste management to solid state fermentation. My primary interest is the environment, the quality of our living resources, and the ways that bacteria can help to manage and degrade toxic wastes and restore environmental health. Consequently, he is very interested in genetic adaptation processes in bacteria, the mechanisms by which they deal with toxic substances, how they react to pollution in general, and how we can apply microbial processes in a useful way (like bacterial bioreporters). One of our major interests is to study how bacteria evolve and adapt to use organic pollutants as novel growth substrates. Bacteria with new degradation capabilities are often selected in polluted environments and have accumulated small (mutations) and large genetic changes (transpositions, recombination, and horizontally transferred elements). His work has been focused to assess the impact of industrial pollution on microbial diversity of wastewater following

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cultivation-dependent and cultivation-independent analysis. His major work involves isolation, screening, identification, and genetic engineering of high impact of microbes for the degradation of hazardous materials. He has more than 200 research publications in highly reputed national and international journals. He directs the research program at Enviro Technology Ltd., Ankleshwar. He has guided more than 100 postgraduate students in various disciplines of life science. He is also serving as a reviewer in various journals of national and international repute. He has edited more than 200 books in wastewater microbiology, environmental microbiology, bioremediation, and hazardous waste treatment.

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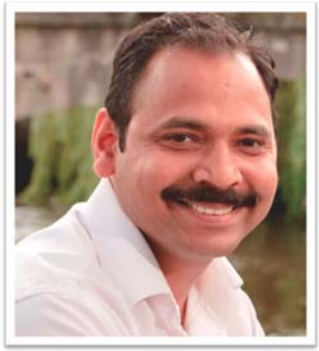
Foreword



Electrochemical technologies are based on the principles of electrochemistry. Electrochemistry deals with the interaction between chemical reactions and electricity. Electrochemistry is concerned with the study of a chemical system involving electron transfer, properties of electrodes, and electrolyte behavior. Electrochemical-driven processes have emerged as efficient and sustainable technologies for the detection and removal of pollutants in water matrices and wastes valorization. This book contains 14 chapters from basic to application of electrochemistry for chemical and biochemical reactions.

The reactions that take place in the electrochemical technologies like oxidation, reduction, phase separation, and biological reactions provide opportunities such as scalability, treatment of diluted and concentrated effluents, and cost-effectiveness. Electrocoagulation, electrodialysis, and electrooxidation can be used to treat wastewater at a faster rate than conventional treatment processes. This book focuses on electrochemical redox processes involved in microbial fuel cell, microbial electrolysis cell, microbial electrosynthesis, enzymatic fuel cell, microbial solar cell, plant microbial fuel cell, and microbial desalination cell. These processes are employed for treating wastewater, moreover generating electricity, producing value-added byproduct and desalination of water.

Overall this book addresses all the technical aspects related to resource management and recommends the application of electrochemical technologies for wastewater management as a sustainable approach. The information provided in this book is fully consistent with the current state of the art with practical information and would be beneficial for the researchers and

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practitioners, who are entering into this highly relevant and important area. I strongly recommend this excellent book to engineers, scientists, students, and industrialists engaged in the sustainable management of wastewater.

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Preface

The field of environmental electrochemistry has emerged as a promising solution to some of the most pressing challenges confronting our planet, including the need for sustainable energy sources and the mitigation of environmental pollution. The degradation of organic compounds of environmental concern has been the subject of a growing number of research studies focusing on different associations with electrochemical degradation processes. Thus, *Advances in Environmental Electrochemistry* is intended to provide the readers with an understanding of the recent advances in environmental electrochemistry, focusing on limited aspects with important developments.

This book provides the basics of environmental electrochemistry, including redox reactions for contaminant removal, mechanism and working principle of different electrochemical reactors. Recent advances and applications of environmental electrochemistry have been thoroughly reviewed and presented in this book. Microbial electrolysis cell (MEC) is a significantly sustainable bioelectrochemical system for biological hydrogen production. MEC is regarded as an environmentally friendly method for producing clean biohydrogen from a variety of waste organic matters and for its low greenhouse gas emissions. Effective biohydrogen production from biowaste in MEC is thoroughly discussed in this book.

Metals are extensively used by many industries such as real estate, mining, construction, and transport. These heavy metals are detrimental to the environment as most of the heavy metals are carcinogenic. Heavy metals can be removed via bioelectrochemical reduction at cathode chamber using the reduction capabilities of bacteria. The feasibility of recovering heavy metals from simulated wastewater in bioelectrochemical systems is discussed in this book.

This book focused on bioelectrochemical systems, electrochemical reactor design and the various electrochemistry-based techniques for practical wastewater degradation, environmental remediation, and bioenergy recovery from waste. Technologies acting as key indicators for addressing the various aspects of environmental electrochemistry are covered, along with comparisons to conventional methods and potential ways forward.

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This book will be of interest to chemical engineers, environmental engineers, and all those interested in environmental biotechnology, bioelectrochemical systems, electrochemical sensors, advanced oxidation processes, biological wastewater treatment, and waste-to-energy recovery.

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Chapter 1

Basics and fundamentals of the mechanisms of electrochemical reactors

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Abstract

Nexus concept is the interconnection between the resource's energy, water, food, land, and climate. Interconnections between the Nexus sectors may benefit from climate change, energy demand, among others, to sustainable development goals (SDGs) through the integrated planning and management processes. Seventeen SDGs were established in several subject areas, such as water, energy, climate, oceans, urbanization, transport, science, and technology, to achieve it. At the same time, materials science has considerably contributed to the accomplishment of several SDGs, according to report maps of the most current sustainability initiatives and research within each SDG area. Advanced materials, for instance, may aid in achieving development objectives in key areas of focus on zero hunger, good health and well-being, clean water and sanitation, affordable and clean energy, industry, innovation and infrastructure, sustainable cities and communities, responsible consumption and production, climate action, and life below water. Then, the scientific and technological domains may develop and construct practical solutions in materials and their applications by identifying essential insights to open novel branches and landscapes for maximizing social benefits. Within this framework, innovative approaches to design and develop decontamination water technologies have been explored by electrochemistry, electrochemical engineering, and material sciences in themes that aim to increase environmental sustainability and Nexus interconnections. Electrochemical-driven processes have emerged as efficient and sustainable technologies for the detection and removal of pollutants in water matrices and wastes valorization, playing a key role in environmental protection, resources recovery, and climate neutrality, which could be simultaneously achieved when a Nexus applicability is visioned. This challenge is related to the lower production of wastes because

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of the direct use of electron as reagent, the improvements on the electrochemical transformations and, most importantly, because electrochemical processes can be powered with green energies or generate energy sources, contributing to a reduction in the carbon footprint of processes. Then, the integration of electrochemical approaches with materials science and reactors design toward the future of Nexus-technologies will be presented here, discussing the important features of main cell designs and their fundamental and electrochemical reactions.

Keywords
Batch cell; Electrochemical reactors; Flow cell; Materials; Wastewater treatment.

1. Introduction

The trials with the laboratory electrochemical cells are seen as a stage in the scaleup of cells to the many square meter dimensions required for commercial production, and the emphasis is on the engineering elements of cell functioning, according to the literature that is currently available (Caliari et al., 2019; Cotillas et al., 2020; Martínez-Huitle et al., 2023; Van der Bruggen, 2021). Recently, environmental and synthetic electrochemical applications that are performed in flow devices have attracted a lot of attention (Martínez-Huitle et al., 2023; Walsh et al., 2019). In this frame, numerous reports have been published where different water matrices with higher degradation removals and simple syntheses with strong selectivity and conversions have been reported, respectively (Baiju et al., 2018; Divyapriya & Nidheesh, 2021; Karim et al., 2021; Nidheesh, 2015; Nidheesh et al., 2013, 2018; Nidheesh & Gandhimathi, 2012, 2014; Oturan et al., 2018; Varindani et al., 2021; Walsh et al., 2019). As a result, the interest in developing different electrolysis cells for environmental and synthetic organic laboratories has increased to show that these devices are practical, more desirable methods to study the interactions between the different parameters, especially between the anode and the supporting electrolyte or solution components and to find the better strategy for scaling-up the process, translating the electrochemical technology from lab to commercial devices (Cornejo et al., 2020; Martínez-Huitle et al., 2015).

Advanced electrocatalytic materials and reactor designs, scale-up on pilot and full scales, and renewable energy as the driving force behind environmental electrochemical treatments are the focus of recent developments in these processes (Martínez-Huitle et al., 2021a; Rodríguez-Narvá et al., 2021). Most of this research intended to close the technological gaps between the bases and widespread deployment of this technology. The preparation of electrode materials, the designs and development of electrochemical cells, and most crucially the energy needs continue to hinder the adoption of this electrochemical technology (Montiel et al., 2022; Sandoval et al., 2022; Sandoval & Salazar, 2021; Sotelo-Gil et al., 2022). An important barrier to the complete commercialization of this technology is the operational cost (electrode and

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energy cost), in addition, to the installation fee (He et al., 2021; Pointer Malpass & de Jesus Motheo, 2021). However, these potential difficulties can be supered when operating conditions are studied, and the mechanisms of electrochemical reactors with electrochemical reactions are understood (Walsh et al., 2019). Within this framework, the fundamentals and mechanisms of EO processes taken into account the electrochemical cells used in wastewater treatment and their operating conditions will be discussed.

2. Examining the electrolytic cell

Scale-up theory often distinguishes between several scale studies, spanning from the lab-scale to the full-scale, during the evaluation of processes utilizing prototype-physical modeling (Martínez-Huitle et al., 2015, 2023; Walsh et al., 2019). It can be assumed that the four steps to be completed along the road toward the full knowledge and characterization of a process are lab, bench, pilot, and prototype, but other classifications can be found depending on the academic reference (Martínez-Huitle et al., 2023). Since the setup sizes typically rise in this order, there is a prevalent misunderstanding of the size-scale relationship, leading some researchers to believe that the difference between a lab scale and a pilot scale can be determined solely by size (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018). It is crucial to remember that disparities in studies do not arise from differences in size but rather from differences in the information that each study expects to collect from its experimental apparatus (Folgueiras-Amador et al., 2020; Pletcher et al., 2018).

The development of electrochemical technology for the treatment of wastewater can be divided into two categories: (1) the applicability of the technology to the treatment of various types of wastewaters; and (2) the development of electrochemical cells, referred to either as individual components or as the entire mechanical design (Folgueiras-Amador et al., 2020; Mousset & Dionysiou, 2020; Solano et al., 2022). Chemical and mechanical engineers often carry out the second situations while chemists and chemical engineers study the first examples (de Oliveira et al., 2022; Martínez-Huitle et al., 2015; Mousset & Dionysiou, 2020; Rodrí et al., 2018).

2.1 Lab-scale apparatus

These are employed for preliminary analysis during which kinetic or thermodynamic data are looked at along with a process's technical viability (Beil et al., 2021; Martínez-Huitle et al., 2015; Pletcher et al., 2018). This stage allows the comparison of various electrode coatings or the characterization of the impact of anions such as sulfate or chloride on the breakdown of an organic pollutant. In this step, working with synthetic solutions rather than actual wastewater enables reliable measurements and the development of theoretical conclusions about the basics of the processes, without confusing the effects resulting from the various

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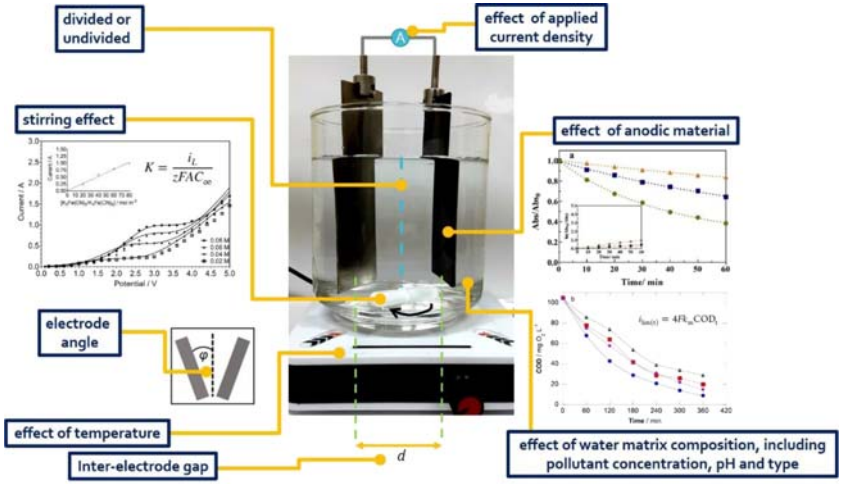

FIGURE 1.1 Overview of crucial but underexplored parameters in some cases, by using a conventional electrolysis cell (Martínez-Huitle et al., 2023).

inputs that are frequently encountered when using actual wastewaters (Brillas, 2014a,b, 2020, 2021; Siré et al., 2021). As already mentioned in authoritative reviews (Brillas, 2014a,b, 2020, 2021; Siré et al., 2014), success at this level depends on a very important characterization from both the electrochemical and analytical points of views. The development of new electrocatalytic materials, the assessment of anthropogenic pollutant degradation in the presence of controlled electrolytes, or the disinfection of various types of pathogens have been the major areas of study in recent years, leading to a very extensive production of scientific knowledge by using different electrochemical reactors (Martínez-Huitle et al., 2021b; Siré et al., 2014).

According to the literature (Martínez-Huitle et al., 2015, 2018a, 2023), there are several factors that affect the performance of the EO-based technologies at small, intermediate, and industrial sizes (Fig. 1.1). These factors include (1) the anode material; (2) the current density; (3) the temperature, (4) the fluid-dynamic circumstances, (5) the supporting electrolyte and conductivity, (6) the pH conditions, and (7) the nature and concentration of the organic pollutant, the dissolved oxygen, and others. These pertinent points should always be taken into account for preliminary research (Arenas et al., 2020; Cotillas et al., 2020; Martínez-Huitle et al., 2023; Walsh et al., 2019).

2.2 Always acting together, the electrode and the operating conditions

A somewhat broad assumption is needed before the idea of the electrolytic cell can be considered. It is common practice to conduct a separate discussion on each electrolysis parameter. This is simply untrue because each parameter affects

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the others, with electrodes' interactions with electrolytes having the most influence. However, other operating conditions can significantly affect the performance of the electrochemical reactor (Martínez-Huitle et al., 2015, 2023).

2.3 Current density and fluid dynamics have an impact

Because these are the only variables that can be directly manipulated, operation current density (i) or, less frequently, applied E_{cell}, are crucial in EO. Interelectrode spacing is fixed and current is continually provided (galvanostatic mode) in EO systems (Arenas et al., 2020; Martínez-Huitle et al., 2015; Walsh et al., 2019). Due to its influence over reaction rate and frequent definition of process efficacy, current density (intensity per unit area of electrode) may be the phrase that is most frequently used (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018). However, additional factors, which are covered below, also affect efficiency. In the low i range, an increase in i often results in greater pollutant removal since the EO is not kinetically constrained by the mass transit of organics to the anode surface (Caliari et al., 2019; Martínez-Huitle et al., 2023). Conversely, a rise in i is anticipated to accelerate O_2 evolution in the high i range (i.e., when the process is mass-transport regulated) (Divyapriya & Nidheesh, 2021; Martínez-Huitle et al., 2015; Nidheesh, 2015; Nidheesh & Gandhimathi, 2012), which will result in a drop in current efficiency (CE) and an increase in energy costs. Higher i values should result in an increase in pollutant removal but also a decline in CE for intermediate i values (i.e., when the process is operating in a mixed kinetic regime) (Mousset, 2022; Nidheesh et al., 2018; Nidheesh & Gandhimathi, 2012; Oturan et al., 2018). This situation may appear straightforward, but as current increases, more oxidants, such as chlorine, ozone, hydrogen peroxide, persulfate, and peroxophosphate, may develop. It is crucial to note that improving the oxidation efficiency or rate does not always result from increasing the current density. The impact of current density depends on the properties of the effluent to be treated as well for a specific anode material (Garcia-Rodriguez et al., 2020; Huguenot et al., 2015; Mousset, 2022; Mousset & Dionysiou, 2020). Additionally, the appearance of the oxygen evolution reaction (OER) and/or mass transport restrictions has been linked to the detrimental effects of growing current density during the EO treatment of specific organic pollutants, as was already indicated (Garcia-Rodriguez et al., 2020; Trellu et al., 2021).

From a critical standpoint, changes in current density could have an impact on how effective the process is, but it is important to keep in mind the other powerful oxidants created at the anode surface. Along with other operating factors (such as dissolved oxygen, pH, temperature, and inorganic ions), the anode's characteristics also have a role in controlling the synthesis of these oxidants (Garcia-Rodriguez et al., 2020; Trellu et al., 2021). As previously mentioned, improper hydrodynamic circumstances can result in the formation

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of mass transport restrictions that influence how current density behaves in EO (Arenas et al., 2020; Garcia-Rodriguez et al., 2020; Martínez-Huitle et al., 2015). One of the most crucial variables when using batch cells is the stirring rate. Proper stirring prevents concentration gradients from forming in the electrolytic cell, guaranteeing uniform conditions (Martínez-Huitle et al., 2023). Additionally, it encourages the transfer of the produced ions, an improvement in the effectiveness of pollution removal, and the transport of the powerful oxidants from the anode surface to the solution (Dunwell et al., 2018; McBeath et al., 2019, 2021). When an electrochemical flow cell is utilized, the distance between the electrodes is decreased and turbulence conditions are increased, which favors a quick interaction of $^{\bullet}OH$ radicals with organic pollutants (Arenas et al., 2020; Garcia-Rodriguez et al., 2020; Martínez-Huitle et al., 2015, 2023; Mousset, 2022; Walsh et al., 2019). The hydrodynamic (turbulent or laminar) conditions in the continuous flow cell, which enabled the efficient elimination of organic matter by $^{\bullet}OH$, then cause the organic matter to be gradually removed even without the addition of electrolytes. From these findings, it can be concluded that a batch reactor is more suitable for lab-scale work because it allows the examination of a variety of operation circumstances (Garcia-Rodriguez et al., 2020). Contrarily, continuous systems are suitable for handling high volumes with an industrialization goal.

Since these factors affect the transit of oxidants and organics and/or the residence time in the cell (Du et al., 2021; Garcia-Rodriguez et al., 2020; Trellu et al., 2021), they have a significant impact on the stirring conditions in batch tank reactors and liquid flow rate in continuous flow systems (Folgueiras-Amador et al., 2020; Gü et al., 2017; Maljuric et al., 2020; Pletcher et al., 2018; Walsh et al., 2019). Finally, it should be noted that fluid dynamics has a significant impact on EO efficiency and it is also directly tied to the design of the cell or reactor.

2.4 Effect of the organic pollutant's nature and concentration

This outcome is specifically connected to the composition of the anode material. The degradation rate and efficiency of the process seem to be mostly unaffected by the type of organic pollutants in the case of "nonactive" anodes, but they are largely dependent on the reactive oxidizing species produced at their anode surfaces. On the other hand, when organic contaminants and their concentrations are changed, it is possible to anticipate various behaviors and efficiencies at "active" anodes (Sibi et al., 2023). The combination of these effects with other operational parameters, such as pH, surface passivation or corrosion, temperature, stirring rate, and potential responses of the organic pollutant at the anode surface (e.g., adsorption/desorption), is crucial to note (Martínez-Huitle et al., 2018b).

The larger the concentration of organic materials to be eliminated, in general, the higher the CE of the process. Contrarily, for low organic loads,

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chemical oxygen demand (COD) declined exponentially, and instantaneus current efficiency (ICE) started to diminish (Labiadh et al., 2015; Martínez-Huitle et al., 2018b; Siré et al., 2014). In this particular situation, COD decreased linearly for large organic loads, but ICE remained constant at around 100%. Based on these findings, a kinetic model that enabled them to forecast the development of COD and ICE for the treatment of organics by EO with BDD (a well-defined nonactive anode) was developed. However, the bulk oxidation of organic compounds using electrogenerated oxidants was avoided since it was expected that the EO of organic compounds would occur quickly (Martínez-Huitle et al., 2018b; Siré et al., 2014). Beginning with the determination of the limiting current density from COD values, the model is created (Panizza & Cerisola, 2009):

$i_{\mathrm{lim}}(t)$ is the limiting current density (A m^{-2}) at time t, 4 is the number of exchanged electrons, k_m is the mass-transport coefficient in the electrochemical reactor (m s^{-1}), and CODt is the chemical oxygen demand (mol m^{-3}) at time t. There are two distinct operational regimes that can be distinguished based on the applied current:

$$I_{lim} = 4FAk_m COD_{(t)} \tag{1.1}$$

(i) $i_{appl} < i_{lim}$: The electrolysis is controlled by the current, which has a 100% efficiency and a linearly decreasing COD over time.

(ii) $i_{appl} > i_{lim}$: Whereas COD removal exhibits an exponential decay due to mass transport restrictions, electrolysis is subject to mass transport control; hence, secondary processes (such OER) occur significantly, resulting in a decrease in ICE.

The equations that defined the time history of COD and ICE were derived from the COD mass balances of the electrochemical reactor and reservoir (Panizza & Cerisola, 2009). Taking into account the aforementioned data, kinetically regulated processes are reached at lower current densities, whereas mass-transport limitation and parasitic O_2 evolution are attained at higher current densities (Martínez-Huitle et al., 2011; Panizza & Cerisola, 2009).

This model's primary flaw is that it ignores the possibility that other chemical species may be involved in various events that occur on the anode surface (Martínez-Huitle et al., 2011). Additionally, it cannot be used with anodes and pollutants that, for a process under current control, do not satisfy ICE = 100%; fortunately, other authors have taken these factors into account and proposed other intriguing theoretical models (Garcia-Rodriguez et al., 2020; Panizza & Cerisola, 2009).

For the sake of simplicity, it has been assumed that the whole oxidation of organic pollutants will take place in competition with the OER, with no

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significant accumulation of intermediates in the bulk. In this instance, both the mass transport and the oxidation reaction control regimes may quickly estimate the ICE for a process operating in galvanostatic mode (De Battisti & Martínez-Huitle, 2018; Garcia-Rodriguez et al., 2020). It was shown that adjusting the current density, flow rate, and beginning concentration of the investigated organic pollutants significantly resulted in a good agreement between experimental data and theoretical predictions (De Battisti & Martínez-Huitle, 2018; Nidheesh et al., 2018; Nidheesh & Gandhimathi, 2012; Oturan et al., 2018; Panizza & Cerisola, 2009).

On the other hand, it has been possible to propose a novel strategy to retain the current efficiency near to 100% even under mass transport limiting conditions by employing mathematical models to predict the EO profiles of organic contaminants (Panizza & Cerisola, 2009). This method states that the working potential is fixed by the nature of the electrode material and is buffered during the oxidation of organic materials. When low CE is reached, a greater electrical charge is required for complete mineralization because a significant quantity of $^{\bullet}OH$ is lost in parasitic nonoxidizing reactions such as the OER. This is due to the effect of the limiting current (Panizza & Cerisola, 2009). When the electrolysis is under mass transport control and the $i_{appl} > i_{lim}$, this behavior is frequently reached. The effective operation of EO of an actual wastewater depends on the estimation of i_{lim} from the COD value using Eq. (1.1) (Martínez-Huitle et al., 2011; Panizza & Cerisola, 2009). The CE and oxidation rate can be increased by using "modulated" electrolysis, which involves adjusting the current density during the electrolysis to get close to the limiting value. It is crucial to note that the mass transport mode in the electrochemical reactor—stirring, flow, turbulence, and so on—has an impact on i_{lim} (Iniesta et al., 2001; Martínez-Huitle et al., 2011; Michaud et al., 2003). Therefore, even though only a few researchers think it is vital, determining the reactor's k_m before usage becomes a crucial parameter to enhance the viability of this advanced oxidation method (Cornejo et al., 2020, 2021; de Oliveira et al., 2022; Martínez-Huitle et al., 2015; Mousset, 2022). It is important to note that i_{lim} mainly influences electrochemical reactions that take place at the electrode surface, such as EO or indirect electrochemical oxidation (IEO), because the primary oxidant ($^{\bullet}OH$ or active chlorine, respectively) is produced during the electrode reaction, which depends on charge transfer and mass transport (Cornejo et al., 2020). The reactivity caused by powerful oxidants once they have reached the electrode surface, in contrast, is not reliant on i_{lim} (Arenas et al., 2020; Beil et al., 2021; Cornejo et al., 2020; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018; Walsh et al., 2019).

By adjusting the organics concentration and current density, it was possible to perform EO on a variety of aromatic compounds in acidic solution (Maljuric et al., 2020; Pletcher et al., 2018). The effectiveness of treatment, however, it might also be impacted by the composition of organic pollutants. However, a change in the pH of the solution may affect the protonated or unprotonated

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versions of organic contaminants' chemical structures, potentially altering their removal rates. The ultimate reliance on the type of electrode must be noted, though, because adsorption and desorption processes are possible once the pollutant's structure has been chemically altered (Martínez-Huitle et al., 2015).

2.5 Effect of conductivity and supporting electrolyte

In electrochemical wastewater treatment, the electrolyte can either be wastewater itself, whether it is raw or modified, or it can be a synthetic aqueous solution that has been particularly prepared to first encourage the synthesis of oxidants before being dosed to the wastewater (Garrido et al., 2008; Martínez-Huitle et al., 2015, 2023). To select divided or undivided cells, this decision is crucial. To achieve concentrations much higher than those found in actual effluents, most lab-scale studies reported in the literature typically use synthetic solutions of a given pollutant (or mixture of pollutants) and high concentrations of salts added as supporting electrolyte to increase the ionic conductivity (Martínez-Huitle et al., 2018a). Sodium chloride or sodium sulfate are frequently added to get the appropriate conductivity value. It is important to note that the Cl-mediated oxidation will be encouraged when chlorides are employed (Martínez-Huitle et al., 2006). However, when using sulfates as an alternative, persulfates can be generated at "nonactive" anodes. It is important to note that the concentration of organic contaminants in these synthetic solutions is not always reasonable (dos Santos et al., 2014). The researched concentrations typically have very high levels, especially for a topical topic at the moment like the depletion of synthetic pollutants such as persistent pollutants that have significant environmental or health interest due to their potential toxicity. The study is main flaw is that it becomes unrealistic, which necessitates cautious management of conclusions, especially if they are intended to be extrapolated to large-scale applications (Garcia-Rodriguez et al., 2020; Marcionilio et al., 2019). However, because it enables researchers to characterize the reactivity and the primary intermediates without significant analytical constraints (in terms of limits of detection and quantification) and avoids significant operational difficulties such as the extreme E_{cell} values and high temperatures as a result of the process, this option is not as bad for a preliminary understanding of the process in terms of the elucidation of reaction pathways (which is the main aim of the lab-scale assessments) (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Panizza & Cerisola, 2009; Pletcher et al., 2018). The actual treatment of wastewater is significantly more complicated. As previously stated, experiments using artificial wastewater are far from the real world, where the industrial process (Espinoza-Montero et al., 2023) used to manufacture the contaminants and salts entirely determines the amounts. Raw wastewater composition changes need to be properly handled. The "intensification" of the concentration is only intriguing from a scientific perspective, as it allows researchers to see if there are any treatment-related variations that might be explained by the switch from a synthetic to a natural water matrix. However, in

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large-scale applications, it makes little sense (Garcia-Rodriguez et al., 2020; Martínez-Sánchez et al., 2022). A source of secondary pollution, adding high salt concentrations to an actual effluent is not a good idea either and should be avoided. Three main options are available if the wastewater conductivity is too low: (1) abandoning the electrochemical route; (2) using specialized microfluidic reactors (see Section 5); or (3) using the electrochemical process as a post-treatment following a preconcentration step such as membrane filtration (Divyapriya & Nidheesh, 2021; Karim et al., 2021; Nidheesh et al., 2018; Nidheesh and Gandhimathi, 2012, 2014; Oturan et al., 2018). Furthermore, although its impact is rarely researched in literature, particulate matter is frequently present in actual wastewater. It proceeds without saying that this kind of fragments could be removed using physical separation techniques to avoid serious operational issues during the electrochemical treatment. In particular, electrolyte flow disruption or electrode fouling could become serious issues in applications utilizing commercial cells with close interelectrode spacing (Mousset, 2022). The composition of the electrolyte may also influence whether membranes or other separators are present in the electrochemical cell. A two-step remediation technique can be developed as an alternative to treating wastewater directly. In the first stage, synthetic solutions can be utilized to electrogenerate oxidants, which are then dosed into the wastewater to reach the chemical oxidation of contaminants (McBeath et al., 2019, 2021). Although there are many studies focusing on the creation of oxidants that may be utilized in environmental remediation, this topic has not yet received much attention, mostly due to the oxidants' stability prior to their introduction into wastewater (Scialdone et al., 2021; Cañizares et al., 2009; Mora et al., 2022). The key benefit of this method is that much more effective treatment may be created by optimizing operation parameters for the formation of oxidants, such as temperature, solution composition, and so on. The electrochemical process and waste treatment are carried out in separate operations, which clearly disadvantages the electrochemical activation of oxidants in the bulk (i.e., the transformation of oxidants into more reactive species, typically radicals formed upon synergistic interactions between electrogenerated oxidants) (Scialdone et al., 2021; Cañizares et al., 2009; Mora et al., 2022; Zhu et al., 2016). The electrochemical activation of oxidants, which can be accomplished by exposure to ultrasound, UV light, or in the presence of H_2O_2, is afterward a crucial step in increasing the effectiveness of the electrochemical wastewater treatment process (Siré et al., 2014; Cañizares et al., 2009; Mora et al., 2022; Zhu et al., 2016; De Araú et al., 2015).

2.6 Influence of pH

In most circumstances, the pollutant removal effectiveness is optimal at an optimum pH value and then decreases at lower or higher pH levels, making the solution pH an essential operational parameter in EO (Panizza & Cerisola, 2009; Panizza et al., 2008; Siré et al., 2014). Since the electroactive species in an

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acidic medium (i.e., the protonated form) can be more quickly oxidized than in an alkaline medium (i.e., the unprotonated form), this behavior is linked to the chemical structure of the pollutant. as well as the decline in the concentration of $^{\bullet}OH$ and other oxidants in the bulk of the solution (ClO/HClO, O_3, H_2O_2, and $S_2O_8^{2-}$) (Martínez-Huitle et al., 2015, 2018a, 2023; Panizza & Cerisola, 2009). When the pH value changes, no particular behavior is observed, making it totally case-sensitive, although it largely affects the IEO process, for instance, when Cl^- ion is present in the medium (Martínez-Huitle et al., 2006, 2015).

2.7 Temperature effect

The impact of temperature on the overall effectiveness of the EO process has not received as much research as other factors, in contrast (Martínez-Huitle et al., 2006; dos Santos et al., 2014). Temperature changes typically have a minor impact on the EO due to the action of hydroxyl radicals (Panizza & Cerisola, 2009). The decrease in medium viscosity, according to some writers, results in a higher mass transfer toward the anode as temperature rises (Panizza & Cerisola, 2009). An improved anode activity may be the primary cause of an increase in temperature's beneficial effects. This is not the case, as increased indirect reactions of organics with electrogenerated oxidizing agents from electrolyte oxidation—particularly when sulfates and chlorides are present in the effluent—are what boost the efficiency in the removal of contaminants (Divyapriya & Nidheesh, 2021; Nidheesh, 2015). However, some oxidants may thermally decompose at high temperatures.

$$S_2O_8{}^{2-} + H_2O \rightarrow 2\ HSO_4{}^- + 12O_2 \tag{1.2}$$

Since this medium is thought to be inert, increasing the temperature has no effect on how quickly it oxidizes. Therefore, the slight change only results from a rise in diffusion rate with temperature due to a fall in medium viscosity. However, operating at room temperature is typically preferable since it allows electrochemical processes to operate with less energy than their non-electrochemical counterparts (such as incineration and supercritical oxidation) (Du et al., 2021; Garcia-Rodriguez et al., 2020; Nidheesh & Gandhimathi, 2012; Trellu et al., 2021). These results support the idea that to get the highest level of oxidation ability, the electrolytic system configuration and variables such as pH and temperature must be optimized.

3. Looking to more realistic conditions

Each one of the operation parameters discussed before has been the subject of a critical discussion on numerous reports (Arenas et al., 2020; Garcia-Rodriguez et al., 2020; Mousset et al., 2017; Walsh et al., 2019). This method is helpful in some circumstances, but it is not completely correct since it ignores potential interactions between the various factors, particularly those between the anode,

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the components of the supporting electrolyte or solution, and the electrochemical reactor (Arenas et al., 2020; Martínez-Huitle et al., 2023; Walsh et al., 2019). The choice of the anode and the nature of the water matrix, which may contain only the organic pollutant and the electrolyte or a combination of pollutants, solvents, inorganic species, and others, have a significant impact on and in the approach, leading to the predominance of particular water-based systems or surface layer processes at the anode (Beil et al., 2021; Folgueiras-Amador et al., 2020; Martínez-Huitle et al., 2023; Pletcher et al., 2018). Additionally, it subsequently has an impact on the bulk volume-based oxidation process.

The investigation with lab scale in batch cells is a step in the right direction because it still uses lab-scale materials and is done so under extremely controlled circumstances while also evaluating flow patterns and integration with other auxiliary operations (Arenas et al., 2020; Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018; Walsh et al., 2019). The formulation of synthetic wastes attempts to approximate the characteristics of real wastewater rather than using pure solutions of pollutants, and in the most advanced steps of this stage, actual wastes may be employed. Some of the objectives of these studies include the impact of operation parameters (commented above) on the process performance, the combination with other processes, the comparison of discontinuous and continuous operation modes, the impact of flow patterns, and preliminary stacking. It is possible to acquire preliminary merit statistics as well as a rough concept of how the process will actually work (Arenas et al., 2020; Martínez-Huitle et al., 2015; Walsh et al., 2019). Although there are many works in which commercial cells prepared for implementation in full-scale applications are used, laboratory materials and equipment are still frequently used at this scale (Jadhav et al., 2024). Mechanical design is also still far from the target (Martínez-Huitle et al., 2015). The power source is connected to the cell using a straightforward method like that used at lab scale, and the instrumentation is similar to that used in a typical research lab. Cells, power sources, and heating/cooling equipment might all be identical to those used in lab settings (Martínez-Huitle et al., 2015). The analytical and electrochemical characterization approaches so lose some of their importance compared with lab scale. The evaluation of whether the small electrodes examined in the lab-scale investigations can be greatly enlarged without incurring a major loss of performance or stability; it is currently a highly fascinating topic (Du et al., 2021; Garcia-Rodriguez et al., 2020; Mousset, 2022; Mousset & Dionysiou, 2020). With these bigger size electrodes, repeatability testing can also be performed. The most important efforts at this scale, however, have been concentrated in recent years on coupling electrochemical processes with other advanced oxidation processes. The most sophisticated of these investigations contrast continuous versus discontinuous operation modes' performance. Additionally, bench-scale investigations have been described in the literature as using tiny cells with electrodes that typically have geometric areas up to 100 cm^2 to

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evaluate actual wastewater (Dewil et al., 2017; Martínez-Huitle et al., 2015, 2023; Montiel et al., 2022; Siré et al., 2014). Numerous of these works try to scale up the system to the pilot level, attempting to approach the standards of what should be the real application based on the experience obtained, ultimately resolving the primary issues related to the use of this genuine waste, without significant evolution on the development of reactors (Cotillas et al., 2020; De Araú et al., 2015; Isidro et al., 2018).

Therefore, the utilization of divided electrolytic cells has drawn a lot of interest recently. When undesirable cathodic processes are to be avoided, ions, gases, by-products, or substrates should not be allowed to migrate (Panizza & Cerisola, 2009; Panizza et al., 2008; Siré et al., 2014). The electrosynthesis of high-value products (at the cathode or anode) and the electrochemical generation of oxidants in a single compartment (at the anode or cathode) are examples of situations in which anodic and cathodic processes need to be separated to favor particular conditions or methods (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018). Then, it is important to choose the implementation, design, and kind of separator. Other important factors that could affect the EO process include the way in which the membranes are stored and the cleaning method.

3.1 Pilot-scale devices

Self-made electrolytic cells and electrocatalytic materials have been used, including flow cells (Fig. 1.2) in divided or undivided configurations, traditional cells with stirring (Fig. 1.1) or stirred tanks, and agitated flasks

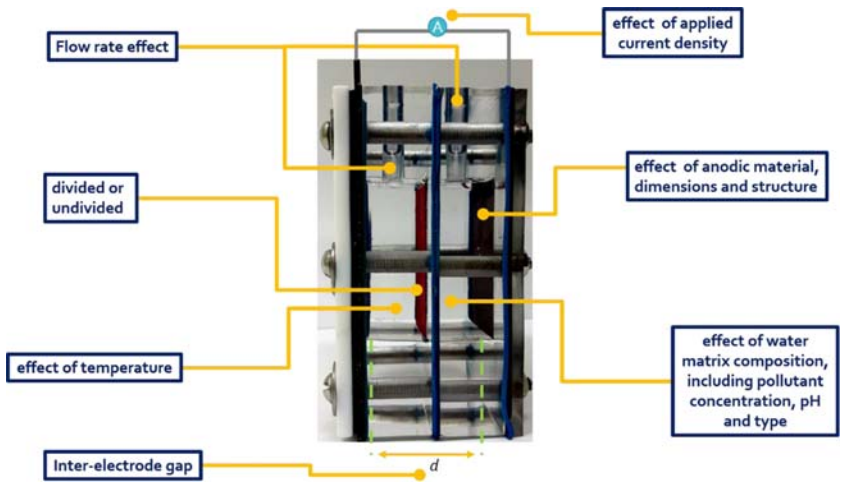

FIGURE 1.2 Overview of crucial parameters when using a flow electrochemical cell (Martínez-Huitle et al., 2023).

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(Beil et al., 2021; Folgueiras-Amador et al., 2020; Martínez-Huitle et al., 2015, 2023). The size and arrangement of the electrodes (angle and distance between electrodes), the shape of the bottom cell (different for beakers, tanks, or conventional cells), the distribution of the electric field (homogenous or heterogenous, which can favor the formation of deposits or polymerization as well as surface corrosion), the preparation and shape of the electrodes, as well as the reactor design are important factors that should be considered when scale up is achieved. In fact, even when cell characterization is not a common technique, it is nevertheless advised for these EO cells to find the mass transfer coefficient (Martínez-Huitle et al., 2015).

Fig. 1.1 shows a typical EO cell, also known as an agitated flask or stirred tank, which is a popular choice in laboratories because of its unique benefits, including dry and secure electrical connections to study the impact of I_{appl} or $E_{cell,}$ an easy method to collect the sample based on predetermined time periods, the addition of the supporting electrolyte or solutions that is simple, the modification of the electrodes (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Martínez-Huitle et al., 2015, 2023; Pletcher et al., 2018) (position, distance, arrangement, and retrieval) that avoids draining the cell, the use of an appropriate mixing and stirring solution that allows the homogenization of the water matrix to improve mass transport by pollutant diffusion/convection toward the electrodes surface and of the intermediates from them, heating using a magnetic stirrer/hot plate for temperature regulation, suitable measurements of the electrode potential and their distribution in the cell, a possible kinetic analysis of water matrices treatment, and easy continuous pH adjustment (Nidheesh & Gandhimathi, 2014).

However, using an undivided stirred tank reactor or undivided beaker has some drawbacks (Brillas, 2014a,b, 2020, 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Martínez-Huitle et al., 2023; Pletcher et al., 2018). Then, the oxidation reaction environment is difficult to scale up because of the following reasons: it appears that the experimental conditions are not entirely fixed; the operation parameters are unpredictable and undefined; the water matrices, effluent, and solution composition are not fully taken into account for EO experiments (Brillas, 2014a,b, 2020, 2021); the control regime (charge or mass transport regime) is not thought to be established by determining the limiting current density (I_{lim}); no fluid dynamics or hydrodynamics analysis was performed to determine the mass transfer coefficient (k_m) (Panizza & Cerisola, 2009); ion strength and conductivity considerations; in the former, ions are added to provide sufficient conductivity, but these ions can also act as oxidant precursors or scavengers; in the latter, similar conductivity values can be achieved using different ion concentrations, which can affect performance. Based on these points, the right factor selection is then required. Because the heterogenous reaction occurs at the anode surface in batch-type electrolysis, mechanical stirring has a significant impact on these results. As mentioned before, mass transport by stirring is essential for moving pollutants,

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intermediaries, and ions to the electrode surface (Martínez-Huitle et al., 2006; Panizza & Cerisola, 2009). However, it has only been weakly investigated. On the other hand, an influence should be anticipated when adjusting the distance between the electrodes. The electrical field distribution, which creates hot-current sites that alter their ability to mineralize organics or to form oxidants, may be related to the electrode distance impact over the EO of organics (Cornejo et al., 2021; Nava et al., 2014; Rivera et al., 2021). Using a precise electrode spacing in this situation would help to ensure electrochemical conversion/combustion in rapid treatment periods and reduce ohmic resistance. Currently, very short interelectrode spacing are advised (Cornejo et al., 2020). Due to their good mas transport conditions, continuous processing, and lower ohmic resistance, flow cells with thin gap or zero gap demonstrate substantial advantages over batch reactors. Additionally, it is feasible to use this sort of flow cells while drastically reducing or eliminating the concentration of the supporting electrolyte (Arenas et al., 2020; Nava et al., 2014; Rivera et al., 2021; Walsh et al., 2019). This makes the use of flow electrochemical cells the better EO tactic for process scaling. The electrosynthesis of oxidants, mass transport, and ionic conductivity are all influenced by temperature, which is advantageous for EO performance (Panizza & Cerisola, 2009; Walsh et al., 2019). However, the use of high current densities raises temperature, necessitating the need of an external cooling jacket.

Due to numerous practical benefits, the traditional plane parallel electrode shape has been heavily adopted into flow reactors (Fig. 1.2). Both theoretically and empirically, the response environment in these cells has been defined, particularly in terms of fluid flow, fluid dispersion, mass transfer, potential distribution, and concentration change. It is advised to choose electrodes well, especially to seek for and test novel materials in significant dimensions. To better understand the impact of competitive reactions, synergistic or antagonistic effects, and the production of oxidants in EO-based technologies, flow reactors should be used to conduct extensive research on critical operation conditions, including materials that are used as anode and cathode and water matrix composition (Panizza & Cerisola, 2009).

However, by comprehending the application of divided or undivided flow reactors based on the choice of the applicability (i.e., the significance of both cathodic and anodic reactions), it is possible to control the cell potential due to the implementation or not of a membrane or separator and, as a result, modulate the production of oxidants, electrical requirements, and costs (Martínez-Huitle et al., 2023).

4. Hydrodynamic conditions

The electrochemical processes can be made more effective by paying attention to the flow pattern (Arenas et al., 2020; Martínez-Huitle et al., 2023; Walsh et al., 2019). As discussed in earlier sections, one of the key issues with several

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electrochemical remediation technologies is that because the majority of pertinent reactions take place on the electrode surfaces; mass species transfer away from and toward the electrode surface is typically the technology's bottleneck (Garcia-Rodriguez et al., 2020). In these situations, the right cell design and selection of the flow pattern are essential for managing this limiting step. Regarding the flow pattern, mixed and plug flow are the two primary models utilized in the engineering of chemical reactors, and they result in the two primary electrochemical cell types used in the scientific literature to remove organic pollutants from wastewater: the mixed tank and the flow cells. The most prevalent substitute for mixed tank cells in the literature is flow cells (Garcia-Rodriguez et al., 2020; Mousset et al., 2017). These cells are frequently used in bench-scale experiments that aim to gather more information on process performance in addition to kinetic data. This enables researchers to debate the technology's potential for use on a larger scale. This type of cells' primary benefit is their improved mass transport capabilities (Martínez-Huitle et al., 2015, 2023), which allow for the treatment of much lower concentrations than mixed cells. However, as will be addressed later in the scale-up section, there are relatively few scientific studies in the literature that are specifically focused on the evaluation of stacking for the removal of organic species, and those that are tend to be limited to a very small number of cells (Beil et al., 2021; Folgueiras-Amador et al., 2020; Maljuric et al., 2020; Pletcher et al., 2018).

When many electrodes are going to be employed in the same cell in electrochemical technology, a special circumstance arises (Cornejo et al., 2021; Nava et al., 2014; Rivera et al., 2021). The decision between a monopolar and a bipolar connection is crucial in this situation. As is well knowledge, all anodes and cathodes in a monopolar connection are directly connected to the power source. In contrast, only the outermost electrodes in a bipolar connection are connected to a power source, and the current that passes through the other electrodes polarizes them. In bipolar systems, the electrode's side that faces an anode is negatively polarized, and the opposite is true of the electrode's side that faces a cathode (Martínez-Huitle et al., 2023). In any case, the few findings look quite promising in terms of lowering energy consumption. Although monopolar configurations have lower operating costs because of the resulting lower cell voltage, bipolar electrodes have been shown to be most effective at removing organic pollutants. Additionally, the bipolar connection enables designers to explore more intriguing mechanical cell designs (Garcia-Rodriguez et al., 2020; Mousset, 2022; Panizza & Cerisola, 2009; Trellu et al., 2021).

Therefore, electrode connection is a fascinating area for future study, and much effort is anticipated in this area. Performance of flow pass cells depends heavily on many construction details, in addition to electrode configuration, turbulence promoters, and interelectrode gap. Use of computational fluid dynamics (CFD) (Garcia-Rodriguez et al., 2020; Jaramillo-Gutiérrez et al., 2020; Rivera et al., 2021; Rodrigues de Oliveira et al., 2012; Simond et al., 1997;

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Wang et al., 2007) tools is anticipated to have a significant impact on the performance of electrolytic cells, similar to what happened with fuel cells over the past 10 years. These tools have not been utilized very often, and the development of cells for the removal of organics is still in its infancy. Finally, several new advances attempt to increase mass transfer by the unique design of the three-dimensional electrodes (including packed electrodes), in addition to the flow pattern optimization that might be derived with CFD (Garcia-Rodriguez et al., 2020). Due to the challenges of expanding their physical aspect to a full scale, they have only sometimes been used for the removal of organics, and no prototypes are worth describing (Nguyen et al., 2024).

5. Remarks

This chapter has given an understanding of the unique characteristics of electrochemical reactors, as well as why and how electrochemical treatments represent a promising alternative for different effluents, from lab to full-scale. First, authors looked at a variety of electrochemical cells for wastewater treatment, with a particular emphasis on lab electrochemical cells for electrochemical treatment of effluents, evaluating their advantages and disadvantages. Particularly for the investigation of operating conditions and the selection of the electrode, applying electrochemistry as a treatment strategy for understanding the mechanisms, oxidants, and behaviors attained in the cells to prove more advantageous. A successful treatment strategy must prioritize cost-effectiveness and process optimization, yet scaling up electrochemical reactors lacks a clear method. Then, the use of flow electrochemical cells was constantly emphasized, giving an overview of the operating conditions that influence their performance. The review stressed the significance of modeling electrochemical processes and the characterization of the flow reactors, as well as the rheological and mass transfer conditions in large-scale electrochemical reactors, because there are actually very few pilot experiments. Electrochemical wastewater treatment can be understood more systematically, and suitable reactors can be constructed by combining different modeling methodologies. Authors identified a crucial parameter, the electrode area over treated volume ratio, which affects energy consumption, costs, and full-scale dimensions. Then, it can conclude that when the wastewater of pollutants is electrochemically treated by using pilot-scale reactors, this process could be suitable by using renewable energies to reduce the specific energy consumption. The wastewater types with the greatest potential for electrochemical treatment should be studied, and their decontamination must be tested in lab- or full-scale reactors. They are particularly well suited for electrochemistry because of a number of benefits, most notably their high salinity, which serves as a source of natural electrolyte and encourages the creation of active species with excellent cleaning and disinfection potential, as evidenced in the operating conditions section. The necessity for high faradaic yields, unpredictability, and the need to

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treat degradation by-products carefully before discharge are also challenges, but these results are associated to the preparation of materials and design, construction, and use of more suitable electrochemical reactors. However, as electrochemistry for wastewater treatment develops, severely contaminated waste streams may offer the best opportunity to showcase the potential of this method on a broad scale.

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Chapter 2

Recent advancements and applications of environmental electrochemistry

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Abstract

For the remediation and disinfection of many classes of wastewaters, electrooxidation (EO) has been widely explored as a decentralized wastewater treatment alternative. It is a green technology with standout benefits including high adaptability, amenability, little chemical addition, and simplicity of use at room temperature and pressure. This technology has proven to be a very effective degradation method for the elimination of various classes of organic pollutants in wastewaters and it is extremely efficient. This chapter provides a summary of the opportunities and difficulties associated with using EO and related techniques to remediate wastewaters. The various anode designs and combinations, as well as the most current developments in anode materials used in EO, were studied. Principles and methods of EO combined with other processes including UV, ultrasonic irradiation, and sulfate radical-based AOPs to increase pollution mineralization were listed, along with their benefits and drawbacks compared with EO alone. Applications of EO and associated processes were reviewed, including electrochemical disinfection, point-of-use, and decentralized water treatment technologies. Critical evaluation of the difficulties and restrictions associated with EO and related technologies have been discussed.

Keywords

Decentralization; Electrochemical oxidation; Fundamentals; Innovations; Oxidants.

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1. Introduction

An efficient treatment option for a variety of organic pollutants, electro-oxidation (EO) (also known as anodic oxidation) techniques have come into use. For the removal of pollutants and pathogens from water, EO-based methods are regarded as adaptable and energy-efficient (Chaplin, 2014; Ganiyu et al., 2020; Martínez-Huitle et al., 2015; Panizza & Cerisola, 2009). This technology has a number of distinct benefits over traditional wastewater treatment methods, such as the capacity to operate at room temperature and pressure, add few or no chemicals, be very versatile, and be flexible enough to adapt to changes in influent composition and flow rate (Ganiyu & Martínez-Huitle, 2019; Särkkä et al., 2015). Because of its adaptability, this technique has found widespread use in environmental remediation. It can also be readily coupled or merged with other methods. For instance, EO has found use in the purification of water, cleanup of sewage, treatment of groundwater, cleanup of polluted soil, and disinfection (Barbosa Ferreira et al., 2020; Martínez-Huitle et al., 2015; Rodrigo et al., 2014; Sirés et al., 2014). Other advanced oxidation techniques as electro-Fenton (EF), sulfite and sulfate radical advanced oxidation, ultrasonication, and ultraviolet irradiation (UV) can be combined with this technology (Ganiyu et al., 2021; Mena et al., 2019; Nidheesh et al., 2022; Souza et al., 2019). EO is interesting and appealing for point-of-use applications and decentralized wastewater treatment due to the small system and flexible architecture.

The capacities of EO for the removal of organic pollutants have been established by a number of bench, pilot, and field size reactors (Martínez-Huitle et al., 2015; Oturan & Aaron, 2014; Särkkä et al., 2015). These studies go into great detail about how to understand basic principles and electrode reactions, as well as about how various operation variables control process performance, how important these parameters are, as well as about kinetics, mechanisms, potential byproducts, degradation pathways, and energy consumption and costs. Due to the complicated composition of real wastewaters, the behavior of EO in synthetic water is frequently different from when the technology is used to treat such wastewaters. Specifically, the chloride and bromide content of actual wastewater is transformed or oxidized, which may result in the generation of harmful organic chloride- and bromide-containing transformation products (Brito et al., 2021; Chaplin, 2014, 2019; Radjenovic & Sedlak, 2015). Additionally, harmful chlorate and perchlorate production may result from EO of chloride-containing effluent (Ganiyu & Gamal El-Din, 2020; Ganiyu & Martínez-Huitle, 2019; Radjenovic & Sedlak, 2015). With little focus on attenuation of specific organic elements, electrochemical treatment in actual wastewaters has mostly focused on removing dissolved organic carbon, ammonia, color, and chemical oxygen demand (Chaplin, 2014; Martínez-Huitle et al., 2018).

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Advanced electrode and reactor designs, scale-ups on pilot and full scales, and renewable energy as the driving force behind EO-based treatments are the focus of recent developments in EO processes (Du et al., 2021; Ganiyu et al., 2020; Ganiyu & Martínez-Huitle, 2020). The majority of these research intended to close the technological gaps between the foundations and widespread deployment of this technology (Jain et al., 2023). The high cost of electrode materials, the creation of hazardous chlorinated and brominated organic intermediates, and most crucially the energy needs continue to hinder the adoption of this electrochemical technology. An important barrier to the complete commercialization of this technology is the operational cost (electrode and energy cost), in addition to the installation fee (Ganiyu et al., 2022; Lacasa et al., 2019).

The potential and difficulties of EO for the treatment of effluents will be discussed in this chapter. The fundamentals and mechanisms of EO processes, coupling EO with other processes, and using EO processes as a point-of-use treatment, decentralized treatment, as well as water disinfection, are covered. Some of the key obstacles preventing the use of these EO-technologies at field scales are operating and installation expenses, the generation of hazardous chlorinated and brominated intermediates, and reactor scaling up.

2. Fundamentals of electrooxidation

The preferred method among the electrochemical advanced oxidation processes (EAOPs) is anodic oxidation (AO), electrooxidation, or EO, as it is often known. AO is the most frequent and straightforward electrochemical technique for the destruction of organic contaminants contained in water. The ability of this electrolytic method to effectively mineralize a wide range of organic compounds in various water matrices, whether created synthetically or using actual wastewater, has been demonstrated. However, the chemical and physical characteristics of the electrocatalytic material (i.e., the anode), as well as a number of operational factors, determine the EO's effectiveness, in terms of water disinfection and decontamination. Due to these drawbacks, it has been unable to fully adopt it as a system at an industrial scale, but over the past 10 years, these limitations have also given rise to new opportunities and difficulties (Martínez-Huitle et al., 2023).

The kind, quantity, and oxidation power of the electrogenerated oxidants are all governed by the anode material. The most significant benefits of the EO approach, such as adaptability, automation susceptibility, viability in mild conditions, moderate energy consumption, and reduced cost, can also be influenced by the operation conditions. Therefore, it is important to describe the principles of the EO treatment of organic contaminants in water. Then, the most widely used "model" and correct electrode/solution interface representations are discussed before moving on to the latest technological developments as well as new insights and novelties that have been recently published in the literature.

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Kuhn (1971), Nilsson et al. (1973), Mieluch et al. (1975), Dabrowski et al. (1975), Papouchado et al. (1972, 1975), Koile and Johnson (1979), and de Sucre (1979) began pioneering work on the EO as a developing alternative for wastewater treatment in the 1970s. Chettiar and Watkinson, as well as Ho, Sharifian, Kirk, and Comninellis, continued these investigations in the 1980s (Chettiar & Watkinson, 1983; Comninellis et al., 1985; Comninellis & Plattner, 1985, 1987; Ho & Chan, 1986; Kirk et al., 1985; Rolewicz et al., 1988; Sharifian & Kirk, 1986). They all made pertinent efforts to research the behavior of various anodic materials by oxidizing various organic contaminants, primarily phenolic compounds and aliphatic acids, with an emphasis on their electrocatalytic activity and electrochemical stability. On the other hand, a major task in the 1990s was the route (or mechanisms) of the EO, in which the organic pollutants are totally decomposed or selectively transformed to other molecules. In fact, Johnson's group was the first to describe the significance of anodic discharge of H_2O in anodic oxygen-transfer reactions and its electrocatalysis (water discharge as a prerequisite of anodic O-transfer mechanisms from hydroxyl radicals concurrently with O_2 evolution) (Chang & Johnson, 1990a, 1990b; Feng & Johnson, 1990; Lowery et al., 1994; Vitt & Johnson, 1992). The research on water discharge and the electrogeneration of hydroxyl radicals at various electrodes were then finished by Comninellis (1994). He provided a condensed process for electrochemical or EO combustion of organics, according to which oxide anodes can be used for selective oxidation and combustion takes place at electrodes that boost the accumulation of hydroxyl radicals on their surface (Fig. 2.1).

This methodology has been applied regularly and consistently in a number of articles and books, leading to both good and negative viewpoints as well as representations or adaptations that have led to misconceptions. Therefore, it is important to remember it.

According to the early Comninellis' model (Comninellis, 1994) (Fig. 2.2), which was published in 1994 for a subset of oxide anodes (MO_x, including Pt, which under O_2 evolution is presented as PtO_x, Ti/lrO_2, and Ti/SnO_2), the electrochemical conversion or combustion of organic compounds occurs upon water discharge as first step, producing adsorbed hydroxyl radicals (reaction (2.1)), and the following results are obtained:

$$MO_x \rightarrow MO_x(\cdot OH) + H^+ + e^- \tag{2.1}$$

The formation of the so-called higher oxide MO_{x+1} may be accomplished in a subsequent phase as a result of an interaction between the adsorbed hydroxyl radicals and the oxygen already present in the oxide anode (reaction (2.2)). This is because oxygen may migrate from the radical to the oxide lattice.

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{2.2}$$

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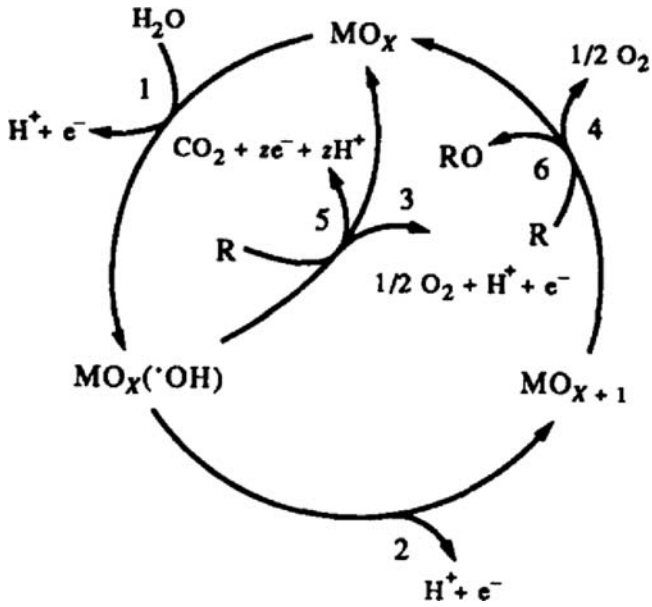

FIGURE 2.1 Generalized scheme of the electrochemical conversion (reaction (2.6))/combustion (reaction (2.5)) of organics with simultaneous oxygen evolution (reactions (2.3) and (2.4)): H_2O discharge (reaction (2.1)); transition of O from ·OH to the lattice of the oxide anode (reaction (2.2)). *Adapted with permission from Comninellis, C. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment.* Electrochimica Acta, 39*:1857–1862. https://doi.org/10.1016/0013-4686(94)85175-1. Copyright 1994 Elsevier.*

Currently, two "active oxygen" states—(1) physisorbed "active oxygen" (adsorbed (·OH)) and (2) chemisorbed "active oxygen" (oxygen in the oxide lattice)—can be taken into consideration. In the presence of oxidizable organic molecules, the physically and chemically adsorbed "active oxygen" should choose different paths (Comninellis, 1994). In conjunction with O_2 evolution (reaction 2.4), the former primarily promotes the complete mineralization of organics (reaction 2.3). In the meantime, the latter should selectively cause the conversion of organics (reaction (2.5)), with the concomitant production of O_2 (reaction (2.6)).

$$R + MO_x(\cdot OH) \rightarrow CO_2 + H^+ + e^- + MO_x \quad (2.3)$$

$$MO_x(\cdot OH) \rightarrow {}^1/_2\ O_2 + H^+ + e^- + MO_x \quad (2.4)$$

$$R + MO_{x+1} \rightarrow RO + MO_x \quad (2.5)$$

$$MO_{x+1} \rightarrow MO_x + {}^1/_2\ O_2 \quad (2.6)$$

This route—reaction information was compiled in a broad scheme (Fig. 2.2). However, it was not until the studies with other electrocatalytic materials (Ti/

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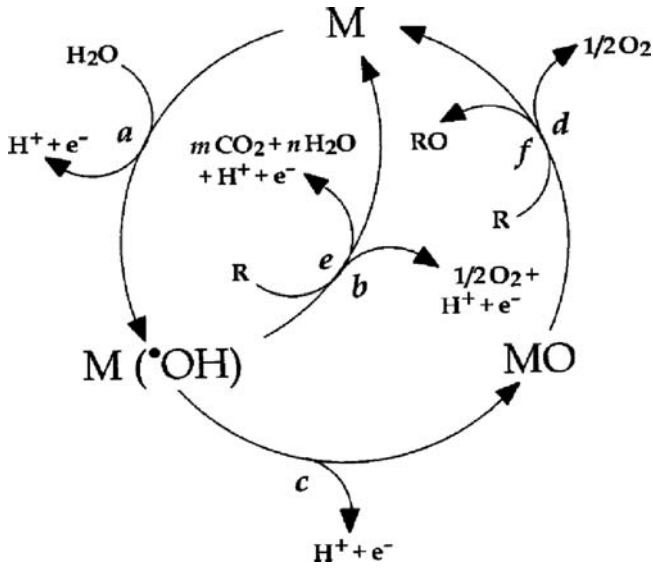

FIGURE 2.2 Scheme of the indirect oxidation of organic compounds with simultaneous oxygen evolution: Water discharge to hydroxyl radicals (path *a*); oxygen evolution by electrochemical oxidation of hydroxyl radicals (*b*); formation of the higher metal oxide (*c*); oxygen evolution by chemical decomposition of the higher metal oxide (*d*); oxidation of the organic compound, R, via hydroxyl radicals (*e*); oxidation of the organic compound via the higher metal oxide (*f*). *Adapted with permission from Marselli, B., Garcia-Gomez, J., Michaud, P. A., Rodrigo, M. A., & Comninellis, Ch. (2003). Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes.* Journal of the Electrochemical Society, 150:*D79–D83.* *https://doi.org/10.1149/1.1553790.* *Copyright Electrochemical Society Inc. 2003.*

SnO_2-Sb_2O_5, PbO_2, and boron-doped diamond (BDD), at the end of the 1990s), that it was possible to utilize the model to distinguish between the two limiting instances of active and inactive anodes (Simond et al., 1997). The type of interaction between the anode surface and the hydroxyl radicals electrochemically produced by the discharge of water and the potential for oxygen evolution offered by each electrode were factors in this classification. Thus, it was established that the process' selectivity and efficiency are significantly influenced by the composition of the electrode material (Marselli et al., 2003).

These findings helped Comninellis (Marselli et al., 2003) (Fig. 2.2) enhance his comprehensive model from the year 2003, which included not oxide anodes as well. Also, direct oxidation was taken into consideration, which results in poor wastewater depollution and is caused by a direct electron transfer to the anode. To achieve a partial or complete decontamination, mediated oxidation via the electrogeneration of oxidizing species (which are

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continuously created) from water discharge or supporting electrolyte oxidation at high applied current (I_{appl}) can also be observed.

It is hypothesized that the oxidation of water from reaction (2.7) results in the heterogenous generation of physisorbed hydroxyl radicals (M(·OH)) at the surface of active and inactive anodes (which are indicated as M). The heterogenous M(·OH) then interacts either strongly or weakly with the anode surface (Marselli et al., 2003).

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \tag{2.7}$$

Only M(·OH) is produced from reaction (2.1) at nonactive anodes due to a weak interaction between the hydroxyl radicals and the electrode surface, whereas for active anodes, a strong interaction of the hydroxyl radicals with the electrode surface is attained, forming the higher oxides or superoxides from reaction (2.8), which are denoted as MO in this model.

$$M(\cdot OH) \rightarrow MO + H^+ + e^- \tag{2.8}$$

It is crucial to note that MO is created as chemisorbed "active oxygen" when higher oxidation states are accessible at the M surface in comparison with the usual potential for oxygen evolution ($E^o = 1.23$ V vs. SHE) (Marselli et al., 2003; Michaud et al., 2003). Then, as a side reaction, it takes part as a mediator through reaction (2.9) in the selective oxidation of organic compounds (also known as electrochemical conversion), which takes place concurrently with oxygen evolution (reaction (2.10)) and affects the effectiveness of the EO process.

$$MO + R \rightarrow M + RO \tag{2.9}$$

$$MO \rightarrow M + {}^1\!/_2\ O_2 \tag{2.10}$$

Physisorbed or free M(·OH) reacts directly with organic molecules, which results in reaction (2.11), which electrochemically incinerates the organic molecules to produce CO_2 and water.

$$a\ M(\cdot OH) + R \rightarrow M + mCO_2 + nH_2O + xH^+ + e^- \tag{2.11}$$

where R is an organic molecule that contains m carbon atoms but no heteroatoms, requiring $a = (2m + n)$ oxygen atoms to completely mineralize to CO_2, and has m carbon atoms. The efficiency of the electrolytic treatment may be greatly impacted by this reaction's competition with the side reaction of O_2 evolution provided by reaction (2.12) (Marselli et al., 2003; Michaud et al., 2003).

$$M(\cdot OH) \rightarrow M + {}^1\!/_2\ O_2 + H^+ + e^- \tag{2.12}$$

The proposed model's reaction scheme in an acidic medium is illustrated in Fig. 2.3, where M stands for an active site on the anode surface (Marselli et al.,

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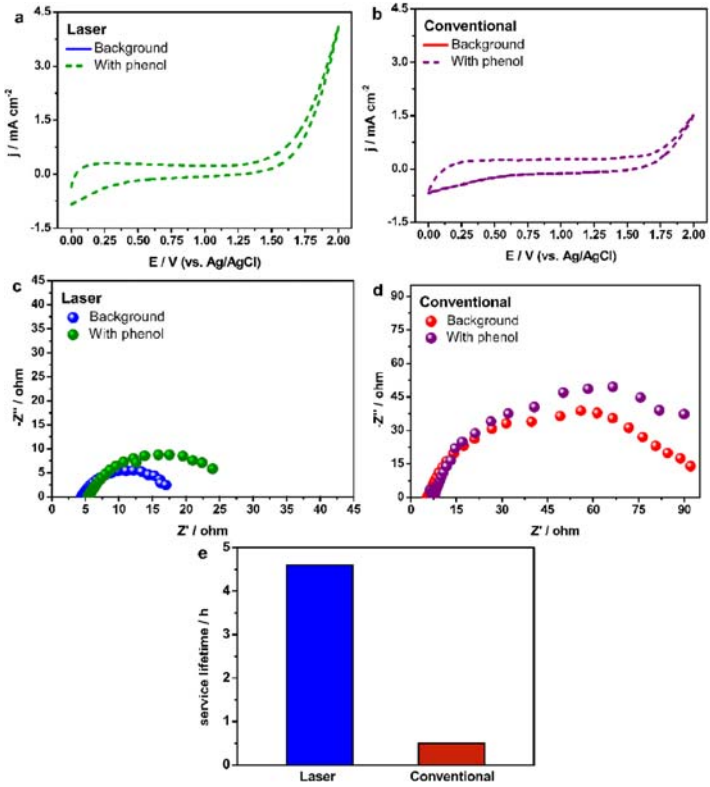

FIGURE 2.3 (A) Cyclic voltammograms for the Ti/SnO_2-Sb anode produced using a conventional furnace and (B) using alternative laser heating recorded at 50 mV/s and (C) Nyquist plots for the Ti/SnO_2-Sb anode produced using a conventional furnace and (D) using alternative laser heating recorded at +1.7 V versus Ag/AgCl and (E) service lifetime of anodes in the 0.1 M Na_2SO_4 background electrolyte. *Reprinted with the permission of Santos, G. O. S., Dória, A. R., Vasconcelos, V. M., Sáez, C., Rodrigo, M. A., Eguiluz, K. I. B., & Salazar-Banda, G. R. (2020). Enhancement of wastewater treatment using novel laser-made Ti/SnO2−Sb anodes with improved electrocatalytic properties.* Chemosphere, 259*:127475.* https://doi.org/10.1016/j.chemosphere.2020.127475.

2003). Modelling suggested that in the reaction cage or in close proximity to the Nernst layer:

(i) Since they do not offer any catalytically active sites for the adsorption of reactants and/or products in aqueous media, no direct engagement of the nonactive anodes in the anodic reaction with organic molecules is anticipated. In other words, the outer sphere reactions and water discharge are the only potential anodic reactions in theory. In the former, there are no significant interactions between the reactants and products and the electrode surface, but in the later, electrolyzable H_2O molecules cover the

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electrode surface and at least one adsorbed layer. The heterogenous hydroxyl radicals created by water discharge, which are engaged in the oxidation of organic contaminants, stimulate electrochemical incineration or burning in the interim (Comninellis, 1994; Marselli et al., 2003);

(ii) At active anodes, organic molecules (reactants or products) directly interact with the anode surface. Because higher oxidation states are available at the anode surface than the thermodynamic potential for oxygen evolution, there is chemisorption of the organic molecules. This is because active anodes provide electrocatalytically active sites. The anode surface oxidation of organic molecules can be mediated in this situation by the surface redox pair MO/M, promoting a selective oxidation or electrochemical conversion (Comninellis, 1994; Marselli et al., 2003; Michaud et al., 2003).

The bond strength between the anode (M) and ·OH is therefore directly related to the chemical reactivity (i.e., rate of oxidation of organic compounds with electrogenerated hydroxyl radicals) and the electrochemical activity (i.e., overpotential for oxygen evolution), allowing the establishment of a general rule: "Weak M-(·OH) interactions lead to low anode electroactivity (i.e., high O_2-overvoltage anodes) and high anode reactivity (fast chemical oxidation of the organic molecules)." However, it is not entirely accurate for all electrocatalytic materials, though, as several unique anodes, created and described in the next section, have demonstrated the coexistence of both direct and indirect oxidation methods.

3. Recent advances in electrode materials and designs in electrochemical oxidation

The "active" and "nonactive" anode materials used in EO are divided into conventional and commercially accessible electrodes. Due to the strong interaction of the produced oxygen species at the electrode surface, the former includes platinum, titanium, and mixed metal oxide electrodes (RuO_2, IrO_2, Ta_2O_5, and their mixture) with low oxygen evolution potential and scarcely mineralize organic contaminants (Barbosa Ferreira et al., 2020; Chaplin, 2014). Due to the abundance of weakly sorbed free hydroxyl radicals (·OH) generated at their surface as a result of water oxidation, the latter has a high oxygen evolution potential (BDD, doped tin and lead oxide, TiO_2 nanotubes, and suboxide TiO_2) and a strong oxidation ability for the complete mineralization of organic contaminants (Chaplin, 2014; Panizza & Cerisola, 2009).

The focus of recent research on "active" electrodes has been on creating extremely electrochemically active electrodes either by doping/coupling with other metals or through new synthesis techniques for mixed metal oxides (Naaz et al., 2024). For instance, compared with pristine electrodes, Sb-, Ta-, Ti-, and Ce-doped active electrodes demonstrated superior electrochemical

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characteristics and degradation efficiency (Wang et al., 2021). The key innovation in improving the electrochemical characteristics and pollutants degrading efficiency has been the development of novel synthesis techniques. One innovative way for creating mixed metal oxide (MMO) electrodes is carbon dioxide (CO_2) laser technology (Santos, Dória, et al., 2020; Santos, Vasconcelos, et al., 2020). By dissolving metallic chloride ($SnCl_2$, and $SbCl_3$) in citric acid and ethylene glycol (EG) at 90°C, a precursor solution is prepared. The solution is then dispersed over both sides of processed Ti plates. At an instantaneous temperature of 600°C, coated plating was heated using a laser (Santos, Dória, et al., 2020). In comparison with conventionally produced electrodes, laser-prepared Ti/SnO_2-Sb displayed better and higher oxygen evolution potential, smaller semicircles on Nyquist plots, and a longer service life (Fig. 2.3). Similar outcomes were attained by heating a Ti/$Ru_{0.7}Ti_{0.3}O_2$ mesh produced for use in a microfluidic flow-through reactor with a CO_2 laser (Santos, Gonzaga, et al., 2020). Another recent development in the preparation of extremely stable and active MMO for electrochemical wastewater treatment is microwave heating assistance technology. By employing microwave heating instead of a furnace, this approach enhances the Pechini method, which is frequently employed for MMO synthesis (Gonzaga et al., 2019, 2020). To create MMO, the precursor solution is made using the Pechini technique. In a typical synthesis, citric acid is added after heating EG to 60°C. Then, at 90°C, metallic salts are added to the mixture while being mechanically stirred, ensuring complete salt dissolution. The substrate plate is heated in a hybrid microwave (microwave aided) rather than a furnace (traditional) after the precursor solution has been painted on it. Different MMOs have been created using this technique, including Ti/$(RuO_2)_{0.5}(IrO_2)_{0.5}$ (Gonzaga et al., 2020), MMO-Ti/RuO_2IrO_2 (Gonzaga et al., 2021a, 2021b), and MMO-RuO_2TiO_2 (Gonzaga et al., 2022), all of which have shown better electrochemical characteristics and performance during EO treatment of wastewaters.

For EO applications, titanium oxide—based nonactive anodes have made significant progress. Magneli phase substoichiometric TiO_2 (Du et al., 2021; Ganiyu et al., 2019) and modified TiO_2 nanotubes (NTs) have been the focus of recent developments in this class of electrodes. Ti/TiO_2-NT electrodes are typically made via a (one- or two-stage) anodization method in organic solution, in which TiO_2-NTs are created on a clean, pretreated substrate (often Ti) at high voltage and then annealed at a high temperature (Tian et al., 2018). Another technique for creating Ti/TiO_2-NTs electrodes is to dip-coat (in a single step or many stages) TiO_2-sols made using the sol—gel process on a metallic substrate (Ti) (Zeng et al., 2022). Compared with traditional Ti electrodes, Ti/TiO_2-NT electrodes have improved electrochemical characteristics and activity (Chaplin, 2014). An excellent substrate for the deposition of various electrocatalysts is Ti/TiO_2-NTs. For instance, PbO_2 electrocatalysts were utilized with Ti/TiO_2-NTs as a substrate (Hu et al., 2014; Santos et al., 2018, 2019). The Ti/TiO_2-NTs were made by anodizing clean, pretreated Ti

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plates in a glycerol and water solution at +30 V for 2 h. Using 0.25 M $Pb(NO_3)_2$ + 0.1 M HNO_3 as the electrolyte, freshly produced Ti/TiO_2-NTs were subsequently employed as the substrate for electrodeposition of PbO_2 under galvanostatic conditions (30 mA/cm^2). In comparison with Ti/Pt, the produced Ti/TiO_2-NTs/PbO_2 demonstrated improved electrochemical characteristics and electrocatalytic activity. SnO_2/TiO_2-NTs (Chai et al., 2011), Ti/TiO_2-NTs/Pd (Du et al., 2015), and Fe-TiO_2-NTs/SnO_2-Sb-Ce (Wang et al., 2021) all reported similar processes. The manufactured Ti/TiO_2-NTs/PbO_2 electrodes have been scaled up by extending their geometrical dimensions from 2 to 70 cm^2, enabling for the creation of more specialized EO reactors for treating larger effluent quantities (Santos et al., 2018, 2019).

Similar to normal TiO_2-NTs and even commercial BDD anodes, blue TiO_2-NTs is a Ti-based "nonactive" electrode with improved electrochemical characteristics and electrocatalytic activity (Cai et al., 2019). TiO_2-NTs were produced through a two-step anodization process, first at +60 V for 1 h in an ethylene glycol electrolyte containing 0.2 wt% NH_4F and 2 wt% distilled water, then at +60 V for 4 h in an electrolyte containing 0.1 wt% NH_4F and 1 wt% distilled water, followed by 2 h of annealing at 450°C. To capture oxygen into the TiO_2 crystal lattice and check for defects, blue TiO_2-NT electrode was made by electrochemical reduction of the generated TiO_2-NTs at current density of 5 mA/cm^2 for 5 min in 10% formic acid (v/v) (Cai et al., 2021; Xu, Cai, et al., 2020). The development of Ti^{3+} sites in the blue TiO_2-NT crystal structure led to structural flaws and oversaw the electrode's increased electrochemical characteristics. Compared with commercial BDD (9.8×10^{-15} M), blue TiO_2-NTs produce more ·OH (1.7×10^{-14} M) (Cai et al., 2019).

Phase of Magnéli, the interesting alternative nonactive electrode TiO_2, sometimes referred to as substoichiometric titanium oxides (sub-TiO_2), has been intensively explored over the past 10 years and competes with BDD anode in terms of electrochemical characteristics and activity (Chaplin, 2014; Ganiyu et al., 2016). Ti_3O_5 is a significant photonic material (Ertekin et al., 2015), whereas Ti_4O_7 has the highest electrochemical characteristics and electrocatalytic activity (Chaplin, 2014; Ganiyu et al., 2017). This class of electrodes has the general formula Ti_nO_{2n-1} ($3 \leq n \leq 9$). Several reduction processes, such as carbothermal reduction (Du et al., 2021; Ganiyu et al., 2016), molten salt synthesis (Wang et al., 2017), cathodic electrochemical deposition (Ertekin et al., 2015), spark plasma sintering (Zhang et al., 2014), and high temperature H_2 reduction (Geng & Chen, 2016), are used to create Ti_4O_7 electrodes from TiO_2. In each of these methods, TiO_2 is converted to Ti_4O_7 with the addition of additional phases as impurities. The conductivity and electrochemical characteristics of the electrode improve with increasing Ti_4O_7 concentration. The amount of the Ti_4O_7 phase is increased by post-synthesis processes including high-temperature plasma elaboration and spark plasma sintering (Ganiyu et al., 2016). Compared with BDD anode, Ti_4O_7 had somewhat worse electrochemical characteristics and electrocatalytic activity,

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but it is much less costly, and the raw ingredients are more readily available (Geng et al., 2015).

Although thin-film BDD anode is a well-established commercial electrode, there are currently few attempts being made to enhance its electrochemical capabilities for wastewater treatment. However, several recent developments have a diamond composite anode as their main emphasis (Jian et al., 2021). For various uses, composite diamonds such metal−diamond (Li et al., 2021), alloy−diamond (Liu, Pei, et al., 2020), sp^2 carbon/sp^3 diamond (Yue et al., 2020), and organic diamond composites (Meng et al., 2018) have recently been produced. Recently, the degradation efficiency was increased by metal compounds or sp^2 carbon diamond composites when were used in electrochemical wastewater treatment (Xu, Yokota, et al., 2020). The diamond composites have an improved oxygen evolution overpotential, a decreased R_{ct}, and larger active regions due to the synergistic relationship between the diamond and the composite counterpart (Liu, Sun, et al., 2020). For instance, the SnO_2/BBD composite demonstrated a higher oxygen evolution overpotential, good conductivity, and excellent electrocatalytic activity (Chai et al., 2018), while the Au/BDD composite demonstrated a fast adsorption kinetics, high active surface area, low resistivity, and high degradation efficiency during EO of pollutants (Chai et al., 2017). Diamond composites' adsorption capacity, background currents, potential windows, and electron transfer kinetics are all greatly impacted by the amount of sp^2 carbon present (Ganiyu et al., 2021; Ganiyu & Martínez-Huitle, 2019; Garcia-Segura et al., 2015). The sp^2 carbon content of diamond composites (Brito et al., 2015; Divyapriya & Nidheesh, 2021) and their electrochemical degradation applications (Medeiros de Araú et al., 2014) have an impact on the electrocatalytical activity and potential of these electrodes for the sulfate and chloride evolution.

Researchers have looked at various electrode designs and arrangements in an effort to improve the efficiency of EO processes through improved mass transfer, increased electroactive surface area, and electrocatalytic reactivity (Martínez-Huitle et al., 2015). Some of the designs that have been used to improve the anode performance in EO wastewater treatment include mesh, rod, disc, tubular, particle, and porous electrodes. For the simultaneous filtration and oxidation of organic contaminants in wastewater, porous reactive electrochemical membranes in a variety of forms, including plate, tube, and disc designs, have recently been developed (Pan et al., 2019).

4. Coupling EO with other advanced oxidation processes

EO is simply used with other advanced oxidation treatments to increase the effectiveness of the latter and shorten the treatment period. EO has been effectively paired with AOPs such UV radiation, ultrasonic assistance, and sulfate radical AOPs (Ganiyu et al., 2021). To improve pollutant breakdown, UV-assisted EO includes irradiating the electrolytic reactor during

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electrochemical wastewater treatment. The increased effectiveness of UV-EO is caused by the activation of electrogenerated secondary oxidants such as persulfate ($S_2O_8^{2-}$), hydrogen peroxide (H_2O_2), oxochlorate I (ClO), and ozone (O_3) by UV irradiation into strong reactive species such as $\cdot OH$, $SO_4\cdot^-$, and $Cl\cdot$, which can speed up the mineralization and degradation of organic pollutants (dos Santos et al., 2017; Souza et al., 2014) (Eqs. 2.13–2.16).

$$H_2O_2 + hv \rightarrow 2\ \cdot OH \tag{2.13}$$

$$H_2O + O_3 + hv \rightarrow 2\ \cdot OH + O_2 \tag{2.14}$$

$$S_2O_8^{2-} + hv \rightarrow 2\ SO_4\cdot^- \tag{2.15}$$

$$ClO^- + hv \rightarrow O\cdot^- + Cl\cdot \tag{2.16}$$

Sono-electrolysis, also known as ultrasound-assisted EO, uses ultrasound to aid in the EO procedure. The secondary effect of ultrasound, known as ultrasonic cavitation, as well as how these phenomena (Eqs. 2.17–2.20) activate electrogenerated secondary oxidants, improves the efficiency of the linked processes (dos Santos et al., 2017).

$$H_2O +))) \rightarrow \cdot OH + H\cdot \tag{2.17}$$

$$H_2O_2 +))) \rightarrow 2\ \cdot OH \tag{2.18}$$

$$H_2O + O_3 +))) \rightarrow 2\ \cdot OH + O_2 \tag{2.19}$$

$$S_2O_8^{2-} +))) \rightarrow 2\ SO_4\cdot^- \tag{2.20}$$

The electrochemical activation of peroxide precursors such as persulfate (PS), peroxymonosulfate (PMS), and sulfite into potent reactive species such as $\cdot OH$, $SO_4\cdot^-$, $O_2\cdot$, and $^1O_2$ rates up the degradation of the pollutants as well as the EO generated oxidants in the couple process. Prior to electrolysis, the wastewater is mixed with the proper precursor concentration. Sulfite, PS, and PMS precursors are electrochemically activated by cathodic reduction, AO, and catalytic activation in the case of catalytic-EO (Ganiyu et al., 2021). The literature has provided a summary of the processes involved in a few sulfite/sulfate EO-based techniques, and Fig. 2.4 illustrates the fundamental mechanisms.

5. Opportunities of EO for treatment of wastewater

5.1 Decentralized water treatment technology

It is crucial to note that two water supply or treatment scenarios are commonly taken into account when using comparison words in this chapter. First, there is the "centralized" or "business as usual" scenario, in which water is taken from surface-based reservoirs, treated as usual at a distance, pumped to fill adjacent storage facilities, and then given to customers as and when necessary. The used water is collected, piped to another centralized wastewater treatment facility,

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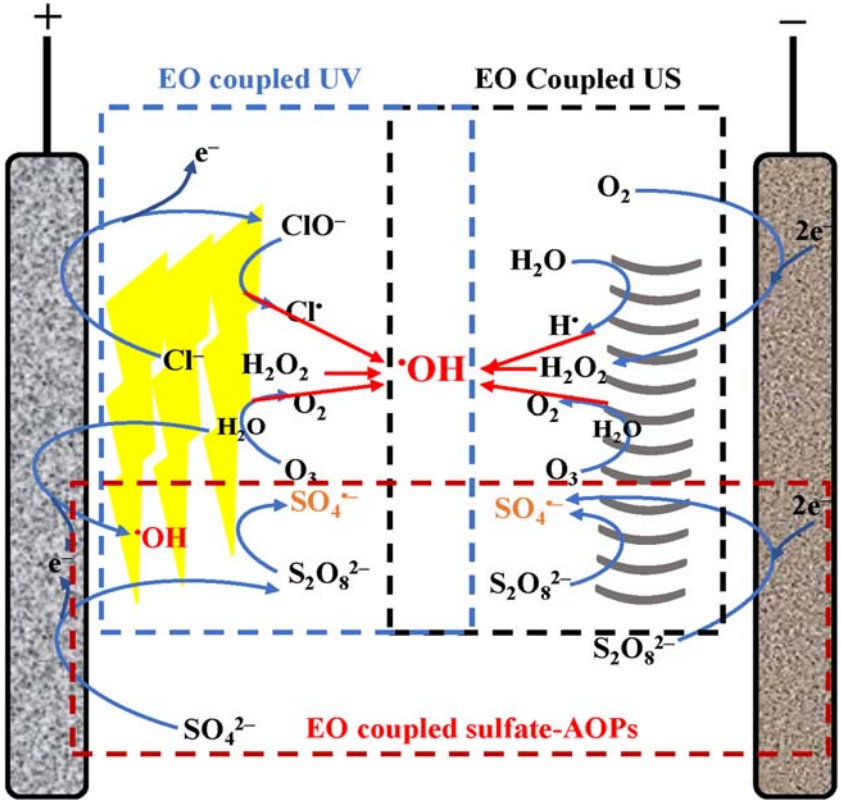

FIGURE 2.4 EO coupled with ultrasound and UV irradiation and SR-AOPs.

where some impurities are removed, and then the effluent is released into neighboring water bodies. The second is a "decentralized" futuristic supply paradigm, in which local water reuse or water treatment technologies are added to the municipal water delivery systems that currently exist in the former or decentralized small-scale water treatment devices in the latter (Mosquera-Romero et al., 2023; Piratla & Goverdhanam, 2015). It is envisioned that each consumption point will contain a treatment unit and some storage space, as shown in various references (Piratla & Goverdhanam, 2015). In terms of treatment techniques that are economically feasible, on-site water reuse is a rising area of study. It is also becoming more popular as a sustainable alternative.

Water provision for domestic, urban, and small-scale industrial use could be planned sustainably by taking into account emerging technologies capable of reducing and reusing the water resources. But to achieve this ambitious goal, two significant challenges must be overcome (Mosquera-Romero et al., 2023): how society views wastewater reuse, and how new water treatment

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technologies and decentralized devices are created. Even while the reuse of wastewater may generate some societal unease, it is important to remember that downstream river influents are occasionally upper-stream wastewater (Piratla & Goverdhanam, 2015). Wastewater treatment plants must follow the correct procedures to ensure water reuse. However, it is challenging to implement the concepts of water recycling at the domestic, urban, or small industrial level due to the vast physical footprint of wastewater treatment plants (Espinoza-Montero et al., 2023; Martínez-Sánchez et al., 2022; Mosquera-Romero et al., 2023).

According to this viewpoint, the development of small, decentralized systems appears to be a feasible alternative for some industries as a substitute for closed-loop water reuse systems in homes (Ganiyu & Martínez-Huitle, 2019; Särkkä et al., 2015) and the automotive sector, notably carwash stations (Espinoza-Montero et al., 2023). The efficient management of water resources may also reduce water consumption and the negative consequences of human activity on ecosystems. For the home or small businesses, decentralized systems must be compact, automated, and easy to use and maintain. To be useful, these systems must also stop the accumulation of waste or biosolids (Espinoza-Montero et al., 2023; Martínez-Sánchez et al., 2022). The primary problem, however, is the large variety of industrial or domestic wastewaters, which may contain solid residues, pigments, or surfactants. The main concern is then how to effectively handle such differentiated water matrices. The creation of small, efficient devices that can handle each of those diverse effluents separately and effectively is a fascinating strategy.

Washing machines are one of the household appliances that utilize the most water in the case of home level (dos Santos et al., 2018; Durán et al., 2018; Ghanbari & Martínez-Huitle, 2019). For every kilogram of clothing, washing machines typically require 6 L of water. Washing machine effluents frequently contain organic colors, textile fibers, and microfibers. In addition to polluting the environment visually, organic dyes may be carcinogenic. Therefore, these dangerous species need to be eliminated from the water if authors intend to use it in closed loops. Meanwhile, one of the small-industry operations that uses a lot of freshwater is vehicle washing, which will profit from recovered wastewater.

However, depending on the quantity of washed vehicles, cleaning agents utilized, and type of dirt, several types of wastewaters are produced. To treat this type of effluents, EO with outstanding performance in the removal of organic contaminants has been proposed and studied. Therefore, given that electrochemical treatment systems are portable and easy to automate, the development of small-scale electrochemical water treatment systems to clean and reuse washing machine effluents or carwash wastewaters may prove to be an intriguing option.

Electrochemical technologies' suitability for treating a real washing machine effluent was demonstrated (dos Santos et al., 2018). The outcomes amply demonstrated that Fenton's electrochemical treatment was superior to

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EO. After 360 min of EO treatment with Pt anodes at 66.6 mA/cm^2, discrete decolorization of 14.9% and total organic carbon (TOC) abatement of 2% were achieved, whereas 55.5% of effluent decolorization and 17.8% of TOC removal were accomplished using BDD anode. This effectiveness was brought about by the BDD surface's effective generation of heterogenous free ·OH. In contrast, the homogenous ·OH produced by the Fenton reaction using the EF and Solar Photo-EF (SP-EF) procedures quickly degraded and decolored the washing machine effluent after 180 min of treatment. EF removed 76% of the TOC after 360 min, but SP-EF eliminated 98% of it after 180−240 min of treatment. As a result, SP-EF is found to be the most effective EAOP for reducing the organic load of washing machine effluents, which is mostly related to organic dyes. However, the need for sunlight delivery systems to the reactors as well as the intricacy of the SP-EF device design may make it difficult to use. Because of the results that showed a proof of concept on the practical application of small-scale electrochemical devices to recycle domestic water sources, the development and upgrading of simpler EO treatments must be investigated and taken into consideration.

To assess the impact of the variable effluent matrix composition (detergent, softener, organic load, water hardness, etc.), additional preanalysis must be taken into account. Although the engineering of this method has been described, technology transfer should come before scaling up and application.

A study on the treatment of carwash effluent utilizing BDD and PbO_2 electrodes in a flow cell with constant operational parameters (current, flow, temperature, and even the electrodes' size) was published by Panizza et al. in the automotive sector (Panizza & Cerisola, 2010). The results showed that organic matter, measured in terms of COD and surfactants, was effectively reduced in 4 h of electrolysis at BDD, whereas COD and surfactants were effectively eliminated with PbO_2 electrodes at a rate of 84% and 72%, respectively. However, after filtering out solid particles, the comparative analysis of electrochemical advanced oxidation processes showed that EF methods are more effective than EO because they can remove more COD.

The parasitic behavior of interactions between ferrous ions and ·OH and the regeneration of H_2O_2 by a potent oxidant that did not react with the organic matter both lower the efficiency of the EF process. The decay of organic matter in terms of COD can be maximized by controlling the amount of Fe^{2+} ions under acidic pH conditions, so encouraging maximum catalytic breakdown of H_2O_2 and subsequently increasing up the ·OH electrogeneration. In this method, ferrous ions, an ideal catalyst, are also easily regenerable. Meanwhile, over 6 h of electrolysis, the EF process using a BDD anode eliminated 96% and 98% of COD at 250 and 500 mA, respectively (Ganiyu et al., 2018).

This finding demonstrates unequivocally that COD removal depends on the current provided to the system; at high currents, COD removal percentage increases as a result of continuous heterogenous ·OH generation at the BDD surface and the mass transport balance (Barbosa Ferreira et al., 2020). In 2 h of

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electrolysis at 500 mA, the EF process removed the surfactants, but the EO process degraded 96% of them in 4 h under the same treatment circumstances. The electrogeneration of H_2O_2 as an oxidant, which contributes to the organic degradation mechanism, is responsible for the decrease in surfactant concentration being attained by EF in shorter time than EO (Ganiyu et al., 2018).

5.2 Point of use treatment technology

Decentralized small-scale water treatment devices based on EO methods proof of concept are an efficient substitute for treating actual home or small-industrial effluents, as discussed in the previous section. A technological diagram for the electrochemical decentralized device, in which water can be recycled in a closed loop, was published in Ganiyu et al. (2018). When electrochemical Fenton-based technology was being examined, it was decided that since the experiment would be conducted in acidic media, acidification and neutralization units would also be necessary. These components can be thought of as consumables that consumers can quickly replace. However, elements such as the iron concentrations and its recovery must be taken into account. In the former, iron contamination may be sparked, whereas in the latter, a poorer catalyst recovery may have an impact on the water quality of subsequent washing cycles. To reduce these issues, potential solutions could be investigated. These specifications are necessary because, in the decentralized system, treated water is anticipated to be recycled in a closed-loop cycle rather than being discharged as effluent. The development of a simpler EO decentralized water treatment unit inside the washing machine, which is turn on/off during the discharged cycles, is therefore encouraged by the complexity of this unit or the needs of additional units (catalyst recovery, dilution catalyst concentration, sunlight delivery system, etc.).

Decentralized systems that enable the creation of point-of-use oxidizing species capable of reaching concentrations on demand are also becoming increasingly necessary to tailor the treatment to the various effluent circumstances (Jadhav et al., 2022). H_2O_2, persulfate, ferrate, peroxocarbonate, and active chlorine are just a few examples of these oxidizing species. Due to the flexibility of specialized applications, small- to medium-sized, compact, and modular machines can be easily adjusted to control the electrolysis conditions and guarantee the appropriate water quality for disinfection and reuse. These promising prospects for the wastewater treatment sector are also anticipated to result in revenue growth soon. In fact, as will be explained in the following, several commercial examples are currently being marketed for use in disinfection treatments.

5.3 Disinfection treatment

One of the key uses of the EO method is the electrochemical disinfection or inactivation of drinking water and wastewater (Martínez-Huitle et al., 2008).

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The several reactive species/oxidants electrogenerated at the electrode site during EO via water/complex matrix electrolysis kill microorganisms (Huang et al., 2016). Bacterial inactivation is brought on by a single or a mixture of free or chemisorbed ·OH, $SO_4 \cdot^-$, $S_2O_8^{2-}$, Cl_2, HOCl/ClO^-, Cl^-, and $ClO_2 \cdot$, depending on the anode material, water chemistry, and current density (Chandra et al., 2022). To show that *Microcystis aeruginosa* was oxidized via the production of active oxidants during electrolysis, Liang et al. (2005) and Xu et al. (2007) employed a Ti-RuO_2 anode. They discovered that the anode materials, current density, reaction periods, and mass transfer had a significant influence on the oxidation suppression of *M. aeruginosa*. In a fixed bed reactor with a 3D conductive diamond anode operating continuously, Zhou et al. (2018) achieved effective electrochemical treatment of water containing *M. aeruginosa*. Additionally, *M. aeruginosa* in the presence of 0.2 mM Fe^{2+} at neutral pH and *Chlorella vulgaris* in the continuous presence of reactive chlorine species were successfully deactivated employing EO using BDD (Long et al., 2017; Mascia et al., 2013). It has also been reported that EO utilizing a monolithic ceramic electrode consisting of magnéli mixed phases of Ti_4O_7, Ti_5O_9, and Ti_9O_{17} deactivated *M. aeruginosa* by 89.2% in 120 reaction times (Gao et al., 2018). Using a mixed metal oxide anode and EO disinfection to treat bacterial-laden wastewater, it was possible to completely inactivate eight different bacteria, including *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Salmonella enterica* (Chandra et al., 2022). The optimal conditions were 2.38 mA/cm^2, 3.33 g/L NaCl, and a 2-min of treatment period. Complete disinfection of stormwater was accomplished by EO employing DSA in 1.3 min at 1.74 mA/cm^2 with a lower energy usage of 0.018 kWh per ton of stormwater treatment (Feng et al., 2018). Despite the low quantity of chloride ions (9 mg/L) in the stormwater, chlorination was discovered to be the primary disinfection method throughout EO treatment. Hypochlorite and chloroamines were found to be the primary reagents for the disinfection process, and a minimum current density of 11.46 A/m^2 was necessary for complete disinfection of *E. coli* wastewater (Cotillas et al., 2016). It has also been shown that the CabECO technology (Cell produced by CONDIAS, Germany) is effective for completely disinfecting wastewater that has been infected with various pathogens (Isidro et al., 2020a). Once more, hypochlorite and chloroamines served as the primary disinfectant reagents.

To expedite the decontamination of wastewater and increase speed and effectiveness, UV disinfection can be coupled with EO. For instance, the comparative effectiveness of UV disinfection, electrolysis, and photo-electrolysis in the eradication of antibiotic-resistant bacteria *Klebsiella pneumoniae* found in hospital urine was evaluated (Herraiz-Carbon et al., 2021). For all current densities and tested anode materials, the coupled EO-UV disinfection method achieves the maximum disinfection rates and completely destroys *K. pneumoniae*. Complete inactivation was achieved by EO alone using DSA or BDD at 50 A/m^2, as opposed to UV disinfection, which can only

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reduce the population of the bacteria by three orders of magnitude. Similar outcomes were achieved with sonochemical-integrated electrochemical disinfection of *E. coli*, which achieved a 200% greater level of disinfection than sonodisinfection alone (Cotillas et al., 2016). The formation of free radicals in large quantities, shear force caused by ultrasonic cavitation, and breakdown of bacterial aggregation are possible disinfection mechanisms during sonoelectrochemical disinfection (Juretic et al., 2015). These mechanisms encourage the interaction between oxidant species and microorganisms.

Two types of damage to bacterial cells can be used to broadly explain bacterial decontamination during EO and related processes. First, reactive species are produced and attack the components of the cell surface, altering the cell membrane's permeability or destroying the bacteria's enzymatic systems. The second step of bacterial inactivation involves the degradation of intracellular components, particularly the loss of deoxyribonucleic acid (DNA) brought on by this damage to the cell surface (Cho et al., 2010). Damages vary depending on the type of bacteria, their structural differences (gram-positive vs. gram-negative), and the C_t value (concentration of disinfectant and their reaction time) (Chandra et al., 2022).

6. Challenges and limitations of EO and related processes

Due to some technical and financial difficulties, there are not currently many scale-up electrochemical reactors and installations in use, which is hindering the application of this technology on field scales. The technological difficulties, such as electrode development, electrode and reactor designs, and combinations, have been thoroughly studied, and various viable solutions have been put forth in the literature (Lacasa et al., 2019; Radjenovic & Sedlak, 2015). The generation of hazardous halogenated by-products and relatively expensive installation and operating costs, however, continue to be obstacles in the scaling up of EO and associated technologies.

6.1 Installation and operation costs

One of the major obstacles to the industrial and environmental applications of electrochemical waste treatment technologies is the initial cost of the electrochemical waste treatment facility. To enable the industrial implementation of these technologies, it is necessary to lower the installation and running costs as well as the costs associated with the electrode material (anode), energy consumption and costs, reactor vessel, and other accessories. Three-dimensional electrochemical reactors and flow-through reactors with three-dimensional electrodes are two techniques that have been shown on bench-scale to significantly improve performance and use less energy than traditional two-dimensional reactors (Ganiyu et al., 2022; Martínez-Huitle et al., 2015). Another alternative endeavor to lower energy and operational costs of these

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technologies is to use renewable energy (solar photovoltaic and wind energy) —driven electrochemical technology, where solar or wind energy directly or indirectly (through energy storage) powers electrochemical reactors (Ganiyu et al., 2020). A few somewhat less expensive alternatives to BDD, which is the most effective and stable electrode for electrochemical wastewater treatment while being quite expensive, have been proposed. These include pristine and doped TiO_2-NTs and sub-TiO_2 anodes.

6.2 Formation of toxic halogenated byproducts

When treating halide-containing (chloride, bromide, and iodide) wastewater, electrochemical wastewater treatment systems must contend with the development and accumulation of harmful and recalcitrant by-products. Regardless of the anode materials utilized, some publications have demonstrated the generation of hazardous chlorinated by-products during EO in chloride media (Chaplin, 2014; Radjenovic & Sedlak, 2015). Trihalomethanes and haloacetic acids, which are organic chlorinated by-products, are produced with all anode materials, whereas chlorate and perchlorate, which are inorganic chlorinated byproducts, are primarily accumulated during EO in chloride medium using nonactive anodes, particularly BDD, TiO_2-NTs, and sub-TiO_2 electrodes (Chaplin, 2014; Ganiyu & Martínez-Huitle, 2019). There is caution about using EO using nonactive anodes for the treatment of some industrial wastewater because most industrial effluents and wastewater contain a sizable amount of chloride ions. This is especially true for wastewater that contains elevated concentrations of chloride ions, such as oil process—affected water (Ganiyu et al., 2022), reverse osmosis concentrate (Radjenovic & Sedlak, 2015), and urine-laden latrine wastewater (Isidro et al., 2020b).

7. Conclusion remarks

The treatment of numerous kinds of organically polluted wastewater and contaminated soils has shown considerable possibilities for EO and associated technologies. The development of electrode materials, a crucial component in determining the technology's effectiveness, has advanced significantly. The development of an alternative, high-performance electrode, like BDD, which is relatively expensive but very successful for treating many types of wastewaters, has been the focus of recent research on electrode preparation. Among the recently produced anode materials with comparable electrocatalytic performance to BDD but less expensive are TiO_2-NTs and sub-TiO_2 anodes.

The advanced oxidation methods based on sulfite/sulfate radicals, sonolysis, and other treatment processes can be used with the EO process to increase its efficiency. Even while coupled procedures are more efficient than EO alone, they are less interesting because of the operational costs and energy/chemical costs of the other process.

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Laboratory/bench scale for many types of wastewaters, EO, and associated technologies have been used as decentralized or point-of-use energy efficient and high-performance treatments. EO and associated activities, particularly in chloride media, are effective at disinfecting wastewater. There are not many field-scale EO treatment plants or pilots, but there are several significant obstacles that are preventing these technologies from being fully scaled up and used in industry. Despite several attempts to address these issues on a bench and pilot scales, the high installation and operation costs as well as the creation and accumulation of chlorinated by-products during EO and associated processes continue to be major obstacles to the scaling up of these technologies. To enable the commercial application of these technologies, future studies should concentrate on addressing these difficulties at pilot scales.

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Chapter 3

Microbial electrolysis cells for effective biohydrogen biogenesis from biowastes

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Abstract

The increments of the global population and rapid industrialization have resulted in tremendous fossil fuel consumption and wastes generation including biowastes. In recent years, biohydrogen has been playing a pivotal role in global renewable energy agendas, where the production of biohydrogen has attracted lots of attention compared with other techniques such as fossil-based hydrogen production. The biohydrogen production avenues can be accomplished via two main mechanisms such as light-dependent response (i.e., biophotolysis and photofermentation) and light-independent response (i.e., dark fermentation and microbial electrohydrogenesis cells). The briny trouble that appears in the aforementioned two methods is the higher cost involvement for the unavailability of cheaper raw feedstocks and poor downstream processing. The utilization of biowastes to produce biohydrogen using microbial electrolysis cells (MEC) is an appreciable way forward to tackle this burning consequence. MECs use microorganisms attached to an anode to produce energy compounds such as biohydrogen from biowaste residues, i.e., organic materials. MECs use broad spectrum of microorganisms in anodes and biogenesis energy compounds, i.e., biohydrogen from organic wastes, which indicates the most recent breakthrough at current scenarios. To this end, current summarization focuses on different techniques for biohydrogen production using microbial electrolysis cells utilizing the biowastes along with special emphasis on bioengineering aspects with benefits and drawbacks in existing MEC system.

Keywords

Bioengineering; Biohydrogen; Biowastes; Electrodes; MECs; Renewable energy.

a. Authors are equally contributed to this work.

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1. Introduction

Energy and water are two indivisible resources that have a substantial effect on the development of human civilization (Baruah et al., 2018). In recent days, there is a substantial role in the global demand for energy. A country's economy is heavily reliant on nonrenewable fuel source. Nonetheless, loss of nonrenewable resources, along with rising levels of pollution, has a major negative consequence for the ecosystem. Therefore, the direction of the research has changed toward the production of alternative sources of energy. More experts believe that hydrogen will be the major source of energy in the future. H_2 is considered one of the most desirable energy types because of its numerous advantages as a clean energy, including high energy density, pollution-free combustion products, and renewability. H_2 is simple to store and carry, comes in a number of useful forms, and has the prospective to replace fossil fuels (Wang et al., 2018). As a result, hydrogen generation can have large synergistic effects with favorable environmental consequences. The production of H_2 gas either by natural apparatus or through thermochemical treatment of biomass can be characterized as biohydrogen. Algae and photosynthetic bacteria may utilize sunlight to create hydrogen gas autotrophically from water; however, its efficiency is currently low, and most scientists believe the method will never be practicable given to the high surface area needs. Biological H_2 production has gained importance over traditional systems for two reasons: (1) they may use biowastes as substrates, and (2) they can function at ambient temperature and pressure (Varanasi et al., 2019). Some of the advantages of biological hydrogen generation technologies are the requirement of environmental temperature and pressure, little energy input, and low transportation costs (Parkhey & Gupta, 2017).

Biodegradable waste such as human waste, green waste, animal waste, food waste, garden and park garbage, home food and kitchen waste, restaurants, caterers, and retail establishments, and equivalent waste from food processing companies are all considered biowaste. Biowastes are produced in a range of ways and are rising on a daily basis, presenting a management and disposal challenge. Biowastes are made up of complex carbohydrate polymers (cellulose, hemicellulose, starch) protein, and lipids; aromatic polymers (lignin) may be used as low-cost raw materials for biotechnological energy generation without competing with the ever-increasing food demand (Bhatia et al., 2017). The bulk of material is disposed of in landfills, where it may degrade into pollutants, contaminate the environment, and generate the greenhouse gases, which contribute to global warming (Idehai et al., 2015). To create various forms of bioenergy from biowastes, several biological (such as anaerobic and aerobic digestion, transesterification, fermentation, and microbial fuel cells) and physicochemical (such as incineration, gasification, landfill, and pyrolysis) processes have been used. Anaerobic digestion (AD) is an established process of a collection of microorganisms, breaking down biological material without

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the need of oxygen, and produce biogas (biohydrogen, carbon dioxide, methane) by several stepwise processes such as a hydrolysis, acidogenesis, acetogenesis, and methanation (Bhatia et al., 2018). Methane and carbon dioxide are greenhouse gases, and they effect environment, human health, respiratory problems, as well as climate change by trapping heat. One of the most extensive techniques for producing hydrogen is conventional electrolysis. The creation of hydrogen by electrolysis is unrelated to CO_2 emissions. The goal of this chapter is to give an overview of microbial electrolysis cells (MECs), which are used to produce hydrogen from biowastes.

MEC is a unique and convincing method for producing hydrogen from organic matter, such as wastewater, biowastes, and other renewable resources. Microbial electrolysis is an organic matter-to-green hydrogen conversion technique. The MEC system is a relatively recent method for producing H_2 from organic materials via electrohydrogenesis using an electric current. This method is a modified version of the MFC in which microorganisms called exoelectrogens perform substrate oxidation and electron release to the anode (Nizami et al., 2017). Organic material is transformed into CO_2, H^+, and electrons in an MEC by electrochemically active microbes. These electrons are delivered to the anode and then travel from the anode to the cathode through an electrical circuit with a power source. Hydrogen is created at the cathode by reducing protons. Cation movement from anode to cathode inside the cell makes up for the passage of negative charge outside the cell. This method is insufficient since it requires a big amount of electricity. The utilization of MECs in fermentation enhances substrate degradation, which leads to the creation of hydrogen. MECs are used to encourage hydrogen generation, although methane may be generated in AD. As a result, numerous techniques for inhibiting methanogens in MEC-AD have been proposed, such as exposure to oxygen alamethicin or a chemical inhibitor (2-bromoethanesulfonate) for hydrogen generation. MECs have been investigated for wide range of applications, including the removal of refractory pollutants, chemical synthesis, resource recovery, and biosensors. MEC technology, in lieu, is still in the early stages and confronts significant obstacles in terms of practical large-scale applications. This chapter presents a review on the generation of biohydrogen from biowastes using MECs, how they work, there drawbacks, with emphasis on strategies to increasing the biohydrogen production.

2. MEC for biohydrogen production from biowastes

2.1 Rational for choice of biowaste

Different kinds of waste materials have been applied to generate hydrogen. The most commonly studied waste include different kinds of wastewater (distillery wastewater, cheese whey, palm oil mill effluent, etc.) and agricultural waste (animal manure, rice/corn/wheat straw, etc.), followed by food

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waste, sewage sludge, and MSW. By determining the chemical conformation of waste, the hydrogen yield (in terms of per unit volatile solid [VS] or chemical oxygen demand [COD]) has been calculated. Alibardi et al. (2016) manifest the hydrogen production has a linear correlation with carbohydrate proportion in the waste composition, while proteins and lipids have a negligible effect. Biowastes such as palm oil from mill effluent and sewage sludge generally have a lower hydrogen production compared with other wastes for high content of either lipid or protein. Furthermore, in addition to various waste materials, research has focused on the use of pretreatment to improve the efficiency of hydrogen producing (Yin & Wang, 2015).

A tangled mixture of multiple set of contaminants is termed as wastewater. Wastewater further carries several undesired chemicals and pathogens, which can cause eutrophication and also can create gastroenteritis, various skin infections, and leptospirosis-like diseases (Bhatia et al., 2021). Mainly we treat effluent due to secure downstream users from hazards by applying different physical (grit and flotation) and chemical (neutralization, flocculation, oxidation, etc.) techniques. However, termination of these methods causes sludge generation and secondary water hazard (Tiwari, 2008). Stored water has become more hazardous at that time while it results in increased levels of micropollutants (Guimarães et al., 2016). Biological hydrogen production needs to resolve thermodynamic and environmental matter using effluent for hydrogen generation by synchronous wastewater remedy. Here, biomasses are used like an unprocessed material, organic matter melted in the wastewater have a high energy state, and it forms mechanical combustion difficult.

2.2 Process of biohydrogen production

As energy demand rises, hydrogen has ability to be a proxy and clean fuel replacement of the prevalent ones (Sher et al., 2021). An effective process to resolve matter is to promote commercial and residential effluent utilization for generating bioelectricity. Here are three main ways used to produce biohydrogen: (1) biophotolysis, (2) dark fermentation, (3) photofermentation, and (4) MECs, which are described (Hallenbeck & Ghosh, 2009) briefly below.

2.2.1 Biophotolysis

Biophotolysis has been denoted a biological approach that predominantly dissociates the water molecule at the time while light (photons) is present. This is a degrading way where photosynthetic microbes, namely, few microalgae and cyanobacteria are involved, in which photosystems (PSI, PSII) absorb light energy and its excreting electrons that are passed through a sequence of energy carriers, resulting in lysed water molecules. Biophotolysis of H_2 production is divided into two different ways: (1) direct biophotolysis and (2) indirect biophotolysis.

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2.2.1.1 Direct biophotolysis

Direct biophotolysis is none other than some photosynthetic microbes' 400−700 nm solar radiation for their cell growth absorbed by few microalgae and cyanobacteria (Kumar et al., 2021). When they accept solar radiation, microbes can emit hydrogen via nitrogenase or hydrogenase. Water breakdown occurs with a light energy of 680 nm wavelength during direct biophotolysis. Electrons are moved via PSII and PSI to a likely adequate portion for ferredoxin (Fd) reduction. Firstly, Fd is reduced and then it utilizes via easing of hydrogenase enzyme NADP+ to NADPH, which is responsible for the production of H_2.

2.2.1.2 Indirect biophotolysis

Indirect biophotolysis is a two-step photosynthetic conversion of carbohydrate to light energy in the course of chemical energy. Firstly, applying light energy, oxygen and carbohydrate (starch and glycogen in green algae and cyanobacteria, respectively) are produced (Nagakawa et al., 2019). When N_2 limited an increase in carbohydrate yield, reduction in O_2 amount can be achieved, which subsequently is advantageous for high H_2 yield. Secondly, the conversion of carbohydrate to CO_2 and H_2 with light energy has occurred under an anaerobic condition with less O_2 (Fakhimi et al., 2019). Azwar et al. (2014) discovered that H_2 is produced by green algae and cyanobacteria. They studied biohydrogen production using four cyanobacteria strains: (1) *Desertifilum* sp. IPPAS B-1220, (2) *Synechocystis* sp. PCC 6803, (3) *Phormidium corium* B-26, and (4) *Synechococcus* sp. and discovered significant H_2 production.

2.2.2 Dark fermentation

Dark fermentation (DF) is the process that no longer required light and required microbes that are resistant to dark conditions of carbohydrates under anoxic situations to give H_2 as a resultant product along with acids. By research, it has been proven a wide variety of sugars are found in *Clostridium* spp., and massive production of it is a possible candidate to form H_2 from wastewater at a main economic emphasis. To demolish these microorganisms, heat treatment is done without interfering spore-forming bacteria. There are some other prospective presents including increase in dilution rate or higher activity is shown when pH is decreased in the reactor and there are optimized controlling environmental factors to expand the harvest of hydrogen.

The formation of H_2 contrasts on a comparatively limited final volume, which is equal to H_2 present in effluent. So that, different researchers have carried out two-step methods that cover the expansion of H_2 via methanogenic anaerobic digestion to increase the final energy generation of the process. To enhance the overall hydrogen production, hybrid methods are also applied, through which from feedstock in photofermentation organic acids formed during dark fermentation to generate H_2.

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2.2.3 Photofermentation

H_2 with photofermentation includes decomposition of organic acids among the support of light-dependent, sulfur/nonsulfur, and purple bacteria. Bacterial clusters manage to do photosynthesis as confessed purple sulfur bacteria (Kossalbayev et al., 2020). Organic acids oxidation, by photofermentive bacteria, generates H_2 and CO_2, named as acetic acid, propionic acid, butyric acid, lactic acid, and malic acid. So that, to derive large amount of H_2 yield, the photofermentation process needed two-stage dark fermentation method (Dange et al., 2021). Energy has been utilized by microbes for their growth and is gathered from the production of adenosine triphosphate (ATP) using light through photophosphorylation. It includes *Rhodobacter* species (*Rhodobacter capsulatus, Rhodobacter sphaeroides, Rhodovulum palustris, and Rhodopseudomonas sulfidophilum*). Beside this, some other bacterial communities are used in H_2 production by utilizing nitrogenase and ATP production, such as *Chlorobium vibrioforme, Allochromatium vinosum, Desulfuromonas acetoxidans, Thiocapsa roseopersicina*, and *Chloroflexus aurantiacus*. In this platform, hydrogenases and nitrogenases help these bacteria to produce H_2 from organic acids in presence of solar energy.

2.2.4 MECs

2.2.4.1 Rational for selecting MECs

Exoelectrogens such as the bacteria that can transfer electrons through extracellular mechanism in MECs use anode as an electron sink to oxidize organics and produce protons and electrons. Protons are diffusing through proton exchange membrane (PEM) to cathode and reduced via electron transferred by the external electric circuit to produce H_2. The MEC system unable to work spontaneously due to the thermodynamic boundaries and supplementary energy is required to drive the reduction reaction. From this law, authors can say any carbon fusion that is perhaps digested by the exoelectrogens can be drawn on in anode of MECs. This causes a huge variety of organics sources studied in MECs, ranging from defined pure chemicals to mixture of real wastewaters (Tao et al., 2008). One of the advantages of MECs over other techniques is mild operating conditions. Here, input is needed to drive the H_2 production from acetate, and this is less than 10% of the typical power preferred for water breakdown. So that, the energy cost of H_2 biogenesis in MECs is lowered, while the conventional industrial electrolysis would cost very high.

2.2.4.2 Impact of cathode upon hydrogen evolution

Cathode material selection is the most crucial aspect for the MECs as it acts as the site for the hydrogen evolution. The rate-limiting step here is hydrogen evolution reaction (HER) for the MEC process as it involves the mass transfer between the solid, liquid, and gas interfaces. HER mechanism comprises

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multistep reactions in which the first step is the electrochemical Volmer reaction, which is followed by a chemical Tafel reaction or an electrochemical Heyrovsky reaction. From Volmer reaction (known as the discharge reaction), electron transfer via the external circuit to the cathode is coupled to the proton adsorption from the electrolyte to the cathode, which in turn leads to the construction of absorbed H atom on the electrode surface. The H atom absorbing source is based on the type of material, presence or absence of catalyst, or the experimental conditions. Newly, biocathode uses bacteria as cathode catalysts, which has also been explored in MECs for hydrogen production that serves as a low-cost alternative to the metal-based catalysts (Kadier et al., 2014).

2.2.4.3 Influence of anode upon hydrogen generation

Almost all of the MEC studies directly use the anode of the MFCs to carry out the electrogenic reactions. Usually, these electrodes comprise carbon-based materials such as carbon felt, activated carbon, graphite, etc. Higher current densities have been shown by porous electrodes as compared with planar electrodes, because porous electrodes provide high surface areas for bacteria attachment. However, there is a chance of bounded mass and charge transfer inside the porous electrodes that could strongly affect the growth of bacteria. The anode prevails the microbial community and also plays a crucial role in determining the hydrogen yields of MECs. A vital issue existing in the MECs (mostly membraneless MECs) is the fabrication of methane along with hydrogen because of the presence of methanogens. Homoacetogens have higher growth rate than electrogens, and it also has the ability to grow chemolithotrophically by utilizing CO_2 and H_2. However, prohibiting the growth of nonelectrogenic bacteria is essential so as to obtain high yields of hydrogen from MECs. Various chemical-based inhibitors have been noted in literature such as 2-bromomethanesulfonate (BES) and lumazine. Thus, utilization of these chemicals increases the ruling charge of the process; thus, low-cost alternatives are needed to suppress methanogens (Kadier et al., 2015).

2.2.4.4 Influence of membrane upon hydrogen evolution

MECs of anode and cathode are separated using ion-exchange membranes to maintain the purity of hydrogen gas and further restrict the anode bacteria to consume the electrochemically produced hydrogen. Membranes that are used commonly are proton exchange membranes, anion-exchange membranes (AEM), bipolar membranes, charge mosaic membranes, etc. Beside from purity, other major advantage of using membrane is that it reduces the crossover of fuel and reduces the risk of short circuit. Thus, using membranes has shown a negative effect while working on MECs. They enhance the

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internal tolerance of the system and cause pH imbalance between the two electrodes, and so that it leads to lower current densities at a given applied voltage.

3. Potential advantages and drawbacks of MEC-associated biohydrogen production

3.1 Issues associated with breakdown of biowaste

Substrates play an important role as it is the sole electron donor for the bacteria to oxidize and produce hydrogen. These substrates range from simple substrates such as acetate, glucose to complex substrates such as wastewater and agricultural waste (Kadier et al., 2016). Thus, it is very much important to choose the right substrate to get the maximum hydrogen yield as conversion efficiency depends on what kind of substrate is being used. Although MEC can produce hydrogen from directly using fermentable substrates, in most of the times it results in increasing the fermentation bacteria and decreasing the substrate. A major drawback in MEC is the methanogenesis. High concentration of hydrogen usually leads to the growth of methanogens. As a consequence, purity and yield of hydrogen production is greatly hampered (Logan et al., 2008). In addition to that, other important issues to production of biohydrogen from biowastes are the removal and utilization of by-products (Manish & Banerjee, 2008). Another drawback that arises due to the use of wastewater for MEC feeding is that wastewater has a very low ionic conductivity (Oliot et al., 2016).

3.2 Issue associated with microbial community usage

3.2.1 Pure culture

Pure cultures offer highly controlled environments for studying electron transport mechanism as well as metabolic engineering. Thermophiles or extremophilic microorganisms such as *Shewanella* sp. and *Geobacter* sp., play a dominant role as pure inoculum for hydrogen production (Kumar et al., 2016). This kind of system improves hydrogen production as well as inhibition of methanogens. However, the major bottleneck of using pure culture is that pure culture is the foremost option exclusively when a single substrate is used (Xing et al., 2020).

3.2.2 Mixed culture

As most of the MECs use wastewater, naturally occurring mixed culture of bacteria in waste water is efficiently used as inoculum source. These cultures use a diverse array of substrates and are resistant to various environmental stresses. Thus, use of mixed culture is economically more favorable. But the

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mixed culture can be affected by the reactor configuration, electrode material, and parameters. Homoacetogens are another class of bacteria that convert CO_2 and H_2 to acetate. These bacteria have a higher growth rate than electrogens and cause trouble in H_2 production.

3.3 Issue associated with bioreactor operation

3.3.1 High capital expenses

The most significant stumbling block to MEC's widespread use is its inability to reduce capital costs. This is mainly owing to the high expense of construction materials. Not only that, the substrate used is also very costly. This is the major problem toward the industrial production of biohydrogen using MEC.

3.3.2 Cathode

One of the major stumbling blocks of MEC is the price for the cathode material. Generally, platinum (Pt) is the best choice for cathode in MEC. However, Pt is unsuitable for upscaling given its high cost and bad environmental consequences (Kundu et al., 2013). Another concern with Pt is that it is likely to be poisoned by compounds such as sulfide, causing it to lose its catalytic properties. Moreover, Ca^{2+}, Mg^{2+}, and additional ions those are essential to sustain the biofilm form hydroxide deposits on the cathode. And this alkalization of cathode causes damage to the cathode (Rousseau et al., 2020).

3.3.3 Long-term stability

Another drawback of MEC is the long-term stability. Researchers have shown that MECs' performance deteriorates after a long period of operation (Escapa et al., 2015). Many causes contribute to this performance degradation, including a decrease in anodic biofilm electrochemical activity, deterioration of cathode performance, fouling and deformation of separator materials, and clogging of the system due to excessive biomass and solid contaminants in wastewaters.

4. Production of biohydrogen is improved using MEC as biowaste feedstock

4.1 Increasing the biohydrogen production by managing bioreactor operation

There are different ways to increase the biohydrogen production. One of the finest methods to do this is by managing the MEC bioreactor operations. Use of different membrane and physical or chemical modification of electrode properties are few of them.

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4.1.1 Use of various types of membrane/separator

The general MEC design is consisting of two chambers: an anode chamber and a cathode chamber that are separated by an ion-exchange membrane. While a membraneless MEC is cost-effective and has a higher hydrogen production rate, the main problem is the loss of H_2 purity. Membrane enhances the innocence of the hydrogen produced and prevents microbial hydrogen consumption at the anode. MECs have employed a variety of membranes, the most prevalent of which is a proton exchange membrane (PEM) called Nafion from Ion Power, Inc (Selembo et al., 2009). Beside this, other types of members have also been used in MECs, including AMI-7001, which is an anion-exchange membrane or AEM (Rozendal et al., 2007), nanofiber-reinforced composite proton exchange membrane or NFR-PEM (Chae et al., 2014), forward osmosis membrane (Lee et al., 2015), bipolar membranes, and charge-mosaic membranes (Rozendal, Sleutels, et al., 2008).

4.1.2 Modification of electrodes

4.1.2.1 Cathode modification

Stainless steel, titanium, carbonaceous materials, and other conductive substances are used as the base of the cathode. To accelerate the hydrogen evolution reaction in cathode, a catalyst is required. Generally, the most used catalyst is platinum (Pt). The high price and poisoning by chemicals such as sulfide are two key disadvantages, which have been forced us to look for platinum free alternatives. A comparative overview has been tabulated in Table 3.1.

4.1.2.1.1 Stainless steel alloy Because of their stability, ease of availability, low cost, low overpotentials, and low toxicity to living organisms, transition metals are considered as alternatives of platinum. According to a study conducted by Olivares-Ramirez et al. SS316 was the best cathode material in alkaline media among three different types of stainless steel with different compositions (SS316, SS304, and SS430) (Olivares-Ramirez et al., 2007). According to a study on microbial corrosion by Munoz et al., the HER was increased by deprotonation of phosphate types on SS cathodes and the hydrogen generation rate has been reached to 4.9 $L/H_2/m^2$ (Munoz et al., 2010). In a study with different nickel and SS alloy, Selembo et al. showed that in terms of cathodic hydrogen recovery, the SS A286 outperformed platinum cathodes (Selembo et al., 2009). Stainless steel fiber felt or SSFF is a low-cost, 3D porous filter material with good conductivity and has been employed as a cathode material and is comparable with Pt/CC cathode and superior to stainless steel mesh (SSM) cathode (Su et al., 2016). Kim et al. (2017) studied fabricated SS material with different 3D structures under catholyte recirculation and have shown that MEC with wool had the highest hydrogen generation rate.

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TABLE 3.1 Comparative view on catalysts with their hydrogen recovery and electrochemical responses (use of different cathode materials/catalyst and their performances).

Material/ catalyst	Cathode potential (v)	Coulombic efficiency (%)	Hpr (m^3/m^3 reactor liquid/d)	Cathodic H_2 recovery (%)	References
SS A286	0.9	–	1.50 ± 0.04	61 ± 3	(Selembo et al., 2009a)
SSW	0.9	–	0.06	70 ± 0.01	(Ribot-Ilobet et al., 2013)
SSFF100	0.9	114.7	3.66 ± 0.43	66.56 ± 2.07	(Su et al., 2016)
SSW	0.9	–	1.3 ± 0.3 L-H_2/L/d	95	(Kim et al., 2017c)
PANI/graphene on SSM	0.9	57	0.65	46	(Ghasemi et al., 2020)
Pt on SSM	0.9	64	0.85	49	(Ghasemi et al., 2020)
Ni–Mo	0.6	75	2	86	(Hu et al., 2009)
Ni–W	0.6	73	1.5	75	(Hu et al., 2009)
Ni–Mo	0.6	79	2.1	90	(Hu et al., 2009)
Ni	1.0	68	4.1 L/l_R/d	103.3	(Manuel et al., 2010)
Ni 210	0.6	92.7 ± 15.8	1.3 ± 0.3	79 ± 10	(Selembo et al., 2010)

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TABLE 3.1 Comparative view on catalysts with their hydrogen recovery and electrochemical responses (use of different cathode materials/catalyst and their performances).—cont'd

Material/ catalyst	Cathode potential (v)	Coulombic efficiency (%)	Hpr (m^3/m^3 reactor liquid/d)	Cathodic H_2 recovery (%)	References
Ni 625	0.9	–	0.79 ± 0.27	43 ± 9	(Selembo et al., 2009a)
NF–G	0.8	–	1.31 ± 0.07 mL H_2/mL reactor/d	–	(Cai et al., 2016)
Ni–P	0.7	97.6 ± 2.2	1.42 L/L/d	92.8 ± 4.8	(Li et al., 2017)
NF + G	0.7	64 ± 1.4	1.12 ± 0.06 mol Co/mol COD	135 ± 2.9	(Wang et al., 2015)
Mos_2	0.8	85 ± 5.2	2.72 ± 0.31	100	(Jeon et al., 2018)
MoS_2–EF	0.6	–	0.133	–	(Rozenfeld et al., 2018)
PANI/MWCNT	0.9	72	0.67	75	(Chen et al., 2015)
Pd	0.6	56.0 ± 10.2	2.6 ± 0.5 L/m^2/d	46.4 ± 8.5	(Huang et al., 2011)
N–Fe/Fe_3C@C	0.8	43.6 ± 0.8	0.0181 ± 0.0011 m^3/m^2/d	79.8 ± 8.4	(Xiao et al., 2012)
NF/NiO–rGo	1	56.64	4.38 mmol/L/d	21.16	
NF/$C0_3O_4$.rGo	1	54.67	3.66 mmol/L/d	18.16	

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4.1.2.1.2 Nickel and nickel-based alloys Ni has a lower HER overpotentials than other noble metals and is more stable in alkaline environments (Siwek et al., 2019). Different Ni alloys such as Ni−Mo, Ni−W, Ni−Fe−Mo, Ni−Fe, Ni−Fe−P, Ni−Fe−Co−P, and Ni−Cr can be employed as HER catalysts and are electrochemically or chemically deposited on carbon-based materials (Yang & Hu, 2019; Zhou et al., 2017). Hu et al. (2009) has developed cathodes by electrodepositing Ni−Mo and Ni−W on carbon fiber-weaved cloth. The Ni−Mo cathode outperformed the Ni−W cathode and was comparable with the Pt cathode in terms of HPR. As cathode catalysts, copper sheets coated with nickel−molybdenum, nickel−iron−molybdenum, or cobalt−molybdenum alloys have been utilized in a study by Jeremissae et al. NF outperforms carbon-based supports in terms of mechanical strength and conductivity.

4.1.2.1.3 Carbon-based nanomaterials Carbon nanomaterials such as carbon nanotubes and graphene are frequently utilized in MECs to provide high-performance catalysts (Xiao et al., 2012). The cathode material was made with novel carbon/iron-based composite nanorod (N−Fe/Fe3C) catalysts with graphite carbon as the shell and maximum hydrogen production rate of 4.38 ± 0.11 mmol/L/d was observed (Xiao et al., 2012). Jayabalan et al. have developed hybrid catalysts with nickel oxide−reduced graphene oxide (NiO-rGO) and cobalt oxide−reduced graphene oxide (Co_3O_4-rGO)-coated nanocomposite cathodes to treat sugar industrial effluent.

4.1.2.1.4 Molybdenum sulfide−based materials Molybdenum sulfides (MoS-X) are potential cathode materials for increasing HER since they are chemically stable and very inexpensive. MECs with Mo-Sx catalysts have higher hydrogen production rates than Pt catalyst because at the edges of Mo-Sx layers, hydrogen atoms easily attach to sulfur anions, contributing to a higher HER rate (Kokko et al., 2017). In acidic wastewater, molybdenum sulfide (MoS_2) on various carbon substrates was employed for HER, and an overpotential slightly higher than platinum cathode was found (Kokko et al., 2017).

4.1.2.1.5 Palladium-based materials Palladium has an excellent catalytic performance. The catalytic efficiency of the Pd nanoparticles was nearly 50 folds elevated than that of the Pt black catalyst and cheaper than Pt. So, by codepositing Pd and Au on Ni-foam base material in MEC, effective HER could be achieved (Chorbadzhiyska et al., 2015). Huang et al. used electrochemical deposition to create a carbon cloth-covered Pd nanoparticles cathode that had a lower overpotential than Pt black coated with carbon paper (Huang et al., 2011).

4.1.2.1.6 Biocathode Microbial biocathode can be a potential alternative for the metal-based cathode. When compared with chemical catalysts,

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microorganisms as cathode catalysts have the benefit of being low cost and self-generating. Microorganisms can use the electrode's surface as an electron source to catalyze the reaction of electrons and protons synthesis of hydrogen in a biocathode MEC (Jafary et al., 2015). In Rozendal, Teller, et al. (2008) developed a biocathode by enriching a biofilm of hydrogen oxidizing, electrochemically active microorganisms on a graphite felt anode. Current density of the biocathode was 1.1 A/m^2, while the control cathode (without biofilm) was only 0.3 A/m^2 (Rozendal, Sleutels, et al., 2008). In another study by Jeremissae et al. both the reactions on anode and cathode were catalyzed by the bacteria and cobalt was successfully recovered with acetate and synthesis of hydrogen in biocathode. To increase hydrogen production in single-chamber, membrane-free biocathode MECs, Chen et al. modified the biocathode with PANI (polyaniline)/MWCNT (multiwalled carbon nanotubes) composites.

4.1.2.2 Anode modification

The particular surface area, conductivity, and surface charge of MEC anodes have influenced the biofilm growth and electron transfer. Electrogenic bacteria growth and development are aided by hydrophilic and positively charged surfaces. There are several methods for improving the anode efficiency and increasing the H_2 production by MECs. The comparative overview has been depicted in Table 3.2.

4.1.2.2.1 Carbon-based materials (carbon nanotubes) Increasing the thickness of these porous electrodes restricts biofilm growth due to pore clogging (Blanchet et al., 2016). Fan et al. created graphite disc multianodes coated with gold (Au) and palladium (Pd) nanoparticles. Au nanoparticle−coated anode produced a current density 20 times higher than plain anode while Pd nanoparticles−coated anode produced 50%−100% higher current than normal ones (Fan et al., 2011). Using carbon nanotubes/polyaniline nanostructure composite as anode materials, Qiao et al. demonstrated that CNTs may increase electron transport capability and surface area of electrode. Wang et al. developed a three-dimensional (3D) nanostructure electrode by growing a self-supported N-doped C/Fe_3O_4 nanotubes composite array onto carbon fiber cloth (Wang et al., 2011).

4.1.2.2.2 Metal-based materials The stainless steel, nickel, and copper are also used as anode materials (Sarma et al., 2021).

4.1.2.2.3 Conductive polymer based materials Barbosa et al. inspected the effects of keyhole (phenolic-based), C-Tex (cellulose-based), and PAN (polyacrylonitrile-based) materials as anode and found out that C-Tex is the best anode material among these (Barbosa et al., 2018).

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TABLE 3.2 Use of different anode materials and their performances.

Material	Cathode potential (v)	Coulombic efficiency (%)	Hpr (m^3/m^3 reactor liquid/d)	Cathodic H_2 recovery (%)	References
Graphite granules	0.6	64	1.23	–	(Cheng & Logan, 2007)
Porous graphite felt	1	60	5.6	–	(Sleutels et al., 2009)
Bioanode	0.7	45	7.4 $H_2/m^2/d$	–	(Lim et al., 2017)
GAC	0.8	100	0.82 ± 0.01 mol H_2/mol acetate	–	(Liu et al., 2014)
GAC/caS	1	96.7	0.55	93.7	(Yasri & Nakhla, 2017)
GAC/FeS	1	93.6	0.46	89.1	(Yasri & Nakhla, 2017)
GAC/Fe_3O_4	1	94.8	0.36	84.1	(Yasri & Nakhla, 2017)

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4.2 Increasing biohydrogen manufacturing in MEC by improving process parameter optimization (Table 3.3)

4.2.1 Temperature

Changing temperature during MEC operation causes changes in activity of microbial community, which affects reactor performance (Omidi et al., 2013). H_2 generation with electrogenic microbes has shown that raising the temperature from 35 to 45°C highest yielded 319 mL of H_2/g substrate, which is the highest yield, measured with the help of (COD); nevertheless, raising the temperature from 45 to 55°C yielded only 182 mL of H_2/g substrate (Lin et al., 2008). The majority of MEC research is performed in a room temperature since electrogenic bacteria are predicted to be more active in this environment (Zhang et al., 2014). It should be emphasized that, as electrochemical investigations of water electrolysis have shown, the kinetics of HER are highly influenced by temperature.

4.2.2 pH

The HER at the cathode is pH dependent; pH is the factor that has the greatest influence on performance as a whole of MECs. Any redox potential shift at the cathode might result in large excitation energies (Varanasi et al., 2019). Microbial activity of biowastes is dependent on pH. This is because microbes are sensitive to their surroundings' pH, and even little changes in pH can cause microbial metabolism to change and substrate production for MEC. Because microorganisms are most active in near-neutral environments, most MEC experiments reported running at pH 7. They predicted decreasing the pH of the cathode chamber and raising the pH of the anode chamber would boost hydrogen generation, and anode with a high starting pH improves hydrogen generation at the cathode (kyazze et al., 2010). This is because the effect of proton builds up because electrogenic bacteria metabolism can be minimized at high pH. It is also reported that periodic polarity reversal was used to maintain pH in two-chamber MECs, claimed by the study (Ki et al., 2017). They described the usage of hybrid biotic/abiotic electrodes as, respectively, anode and cathode. This method reduced pH swings, resulting in a 5.3-fold increase in hydrogen generation (Varanasi & Jhansi, 2019). As a result, these investigations underline the need of maintaining an appropriate pH throughout MEC operation.

4.2.3 Applied voltage

In MECs, voltage is the main factor for generating hydrogen from biowastes. If we use more input voltage, then we get more hydrogen. A tiny external voltage (0.2 V minimum) is administrated across the cell to accomplish the thermodynamic barrier. Although 0.2 V minimum is required according to theory, hydrogen evolution at the cathode needs an input potential in the

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TABLE 3.3 Impact of process parameters for biohydrogen production.

Sl No.	Parameters	Description	References
1.	pH	**(i)** Considered the pH ranges 4.5–9 are efficient for biohydrogen production. **(ii)** The pH at 5 decreases the hydrogen formation due to low biomass growth, and the effective production of hydrogen takes place above 5.5 pH. **(iii)** The ideal value of pH 5.5–6.5, which is large production of hydrogen and less yield of solvent. **(iv)** Microbial activities are pH-related; microorganisms have low resistance to pH, which may cause changes in microbial respiration consequently and extracellular electron transfer. **(v)** For the dark hydrogen fermentation, the optimal pH is 5.5–6.5 for efficient hydrogen production for various wastewaters and pure substrates. **(vi)** A huge constant pH range from 4.0 to 12.0 with a pH gap of 1.0 unit was applied to dairy manure fermentation, the highest hydrogen yield was observed at pH 5.0.	(Stavropoulos et al., 2016; Sivagurunathan & Lin, 2020; Ma et al., 2015; Ki et al., 2017; Zhang et al., 2014; Lin et al., 2012; Xing et al., 2010)
2.	Time	**(i)** When decrease the HRT from 12 to 6 h for the degradation of steam exploded liquor. **(ii)** 8–4 h for the degradation of cassava processing wastewater, the hydrogen production formed for the both cases enhanced significantly. **(iii)** Dark fermentation of hydrogen from HRT requires time on between 0.5 and 24 h is based on the substrate and the process used.	(Veeravalli et al., 2014; Rosa et al., 2014; Fernandes et al., 2013)
3.	Temperature	**(i)** The temperature of 30–49°C is efficient for hydrogen manufacturing using mixed culture.	(Lin et al., 2012; Rosa et al., 2014; Dippolito et al., 2010; Omidi

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TABLE 3.3 Impact of process parameters for biohydrogen production.—cont'd

Sl No.	Parameters	Description	References
		(ii) The temperature on between 25 and 60°C hydrogen (H_2) making show effectiveness. **(iii)** From brewery wastewater enhance 25–40°C temperature, the cumulative hydrogen production (CHP) yield and above 45°C the yielding value get affected. **(iv)** COD is removed by microbes loading at the anode, which has 31°C the most structured controlling temperature for MECs. **(v)** Using a single-chambered MEC formed hydrogen at low temperatures such as 4°C, while simultaneously reducing the generation of methane.	et al., 2013; Lu et al., 2011)
4.	Applied voltage	**(i)** A low amount of 0.2 V should be applied to crack the barrier of thermodynamics as defined in the previous sections. **(ii)** Normally, the optimal values observed in MECs are in the scale of 0.2–0.8 V.	(Guimarães et al., 2016)
5.	Nutrient	**(i)** The inorganic salt, e.g., urea doesn't play part of the production of hydrogen. **(ii)** Cornstarch serves as an alternative and works as a peptone supplement. **(iii)** Dark fermentation stabilization process is increased by carbon to nitrogen ratio (C/N ratio) and productivity affected and HPR. The overall hydrogen production will be enhanced by optimum phosphate content. **(iv)** Elements, example: Mg, Na, Zn, Fe, K, I, Co, Mn, Ni, Cu, Mo, and Ca, have certain effects on hydrogen production.	(Yokoi et al., 2001; Yokoi et al., 2002; Lin & Lay, 2004)

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TABLE 3.3 Impact of process parameters for biohydrogen production.—cont'd

Sl No.	Parameters	Description	References
6.	Acid concentration	**(i)** The dominant metabolic products such as acetic acid, ethanol, butyric acid, and propionic acid and the metabolic route can be affected by HRT and OLR. The substrate degradation efficiency, HPR, and HY decrease with enhancing in VFA concentration. **(ii)** The metabolic route can be affected by HRT and OLR.	(Lee et al., 2002; Tchamango et al., 2010)

vicinity of 0.6−0.8 V in practice. The input voltage, which is in turn reliant on the category of substrate being used, determines the energy efficiency process of hydrogen evolution (Call & Logan, 2008).

4.2.4 Fuel sources of MEC

MEC is to obtain almost 100% substrate utilization and a potential maximum yield of 12 mol H_2 per mole of glucose equivalent eaten, but practical yields of 2.5−3.8 mol/mol have been achieved (Escapa et al., 2016). As a result, no one substrate can be considered optimal to produce hydrogen in an MEC reactor, and comparing MEC performance only based on substrate employed is unjustifiable. Substrate flow rate, HRT, organic matter content (e.g., COD), pH, temperature, and external bias are just a few of the operating factors that must be carefully considered. Researchers have studied a variety of reactor designs and material variables, including increasing the active vicinity of the anode and cathode and the suitability of membrane materials (Kadier et al., 2016). Without this previously discussed parameter, some other parameters and various additional factors have an impact on performance of MECs (Patwardhan et al., 2021). For example, it has been found that reducing the separation between electrodes increased hydrogen generation (Cheng et al., 2011). The influence of various buffers on hydrogen generation and solution resistance has also been discussed.

4.3 Increasing H_2 production using MEC improving biowastes recycling or pretreatment approaches

Biowastes recycling refers to biodegradable wastes, composting, and anaerobic digestion, as well as waste management in general (https://www.r-e-a.net/).

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Agricultural wastes offer a terrific way to recover clean energy and chemical products, and they have a lot of promise for biorefinery use (Forster-Carneiro et al., 2013). Complex substrates/feedstocks are not ideal for H_2-generating biocatalysts and represent a significant barrier in the development of biological H_2 production pathways. Many pretreatment procedures were evaluated to convert nonutilizable chemicals into fermentable substrates, dependent on the types of substrates availability. Physical (mechanical pretreatment, extrusion, and pyrolysis), physicochemical (steam explosion, ammonia fiber explosion, CO_2 explosion, liquid hot water, wet oxidation, sonification, and microwave-based pre-treatment), chemical (ozonolysis, acid hydrolysis, alkaline hydrolysis, oxidative delignification, organosolvation, and ionic liquids), and biological (enzymatic hydrolysis) pretreatments are the four major categories. The physicochemical and chemical treatments are the most effective pretreatments for MECs. To boost these qualities even further, several attempts have been undertaken to alter their surfaces (via physical and chemical treatments) to improve microbial adhesion and increase the surface area for electron exchange between microorganisms and the electrode. Different carbon felt electrode pretreatment procedures were investigated (Eisa et al., 2023). Chitosan pretreatment covers the neutral carbon felt with a positively charged layer, enhancing gram-negative cell interactions with the electrode as well as neutral red polymerization, which alters the surface structure of carbon felt electrodes due to the creation of a poly(neutral red) coating, which acts as a redox mediator (Pauliukaite et al., 2007). Pretreatment with isopropanol lowers functional groups, which improves electron transport characteristics and microbial adherence on carbon felt electrodes (Cheng et al., 2017).

Heat treatment with nitrogen or ammonia gas, acid treatment, and surfactant treatment are all pretreatment techniques that can increase anode surface area and improve biocompatibility in MECs (Spiess et al., 2021). Some metals and materials, such as stainless steel, silver, copper, and nickel, may be utilized as MEC anodes due to their higher conductivity than carbon materials. The hydrogen production of the MEC reactor is also influenced by the variation in inoculum. To manufacture biohydrogen from dairy wastewater as an organic raw material, Wong et al. employ pretreatment landfill leachate sludge (LLS) as an inoculum. The maximal H_2 production at pH 6 and 37°C is 113.22.9 mmol H_2/g COD (Wong et al., 2019). Other electrode and electrolyte pretreatment procedures such as ultrasonication, heat shock, and air exposure have been proven to be successful in controlling methanogen in MECs. In MECs, different operating conditions and reactor design modifications may be used to manage methanogenesis and achieve maximum hydrogen output. However, some pretreatments, such as pH, may be required for AD effluent to allow for more effective MEC functioning. Dilution and specific additives can be used to balance the availability of nutrients such as salts, maintain an acceptable feedstock concentration, avoid inhibition, and retain reasonable

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cycle periods, as well as keep superior solution conductivity (Bakonyi et al., 2018). VFA builds up during WAS fermentation (ultrasonic pretreatment) to feed the anode of a 28 mL membrane-less MEC. The cell was run in 24−48 h batch cycles and produced 1.7 L H_2 L/h/d of hydrogen with high energy efficiency (162%), as well as soluble COD removal rates of up to 50%, which improved to 60% when the input was diluted by a factor of 2. Chemical (alkali) pretreatment of WAS to improve hydrolysis has also shown to be a viable solution (Wang et al., 2014).

4.4 Increasing the biohydrogen production by bioengineering

4.4.1 Use of different thermophiles

The employment of thermophilic microorganisms at the anode for mediating bioelectrocatalytic reactions offers various advantages over mesophiles or nonenzymatic and enzymatic electrocatalysts. This includes enhancement of oxidation rate at anode, faster growth rate, higher substrate utilization, and increase in hydrogen yield. Wrighton et al. have discovered that a thermophile (Table 3.4), *Thermincola potens* strain JR, may transmit electrons directly.

TABLE 3.4 Use of different thermophiles and their performances.

Organism	Temperature and pH	Hydrogen yield	References
Activated sludge-based biofilm	–	2.1 mmol/L/d	(Wang, Sheng, et al., 2017; Wang, Zhang, et al., 2017)
Anaerobically digested sewage sludge	–	1.1 mol/mol acetate	(Kyazze et al., 2010)
Thermotoga neopolitana (wild)	80°C, 7.0	3.1 mmol/mmol sugar	(Dreschke et al., 2019)
Thermopolis hot spring consortium (wild)	60°C, 7.0	1.07 mmol/g prairie cord grass	(Bibra et al., 2018)
Caldicellulosiruptor bescii strain DSM 6725 (wild)	78°C, 7.0	4.40 mmol/g volatile solids	(Yilmazel et al., 2015)
Caloranaerobacter azorensis strain H53214 (wild)	60°C, 7.7	1.46 mmol/mmol glucose	(Jiang et al., 2014)
Thermophilic mixed culture (wild)	55°C, 5.5	1.68 mmol/mmol sugar	(Kongjan et al., 2019)

Continued

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TABLE 3.4 Use of different thermophiles and their performances.—cont'd

Organism	Temperature and pH	Hydrogen yield	References
Caldicellulosiruptor bescii (recombinant-ldh-ΔpyrFA, ura-/5-FOA^R)	75°C, 7.0	5 mmol/g switch grass	(Cha et al., 2013)
Thermoanaerobacterium thermosaccharolyticum TERI strain S7 (wild)	60°C, 7.5	2.5 mmol/mmol glucose	(Singh et al., 2014)
Thermoanaerobacterium thermosaccharolyticum strain W16 (wild)	60°C, 7.0	10.8 mmol/g sugar equivalent	(Ren et al., 2010)

According to electroanalytical studies, transfer of electrode biofilms to sterile anoxic MFCs did not alter current output. Yilmazel et al. (2018) studied the electrogenic activity of two iron-reducing archaea, *Ferroglobus placidus* and *Geoglobus ahangari*. Hirano et al. found that increasing the temperature enhances membrane fluidity, which leads to improved electron transport. Lusk et al. studied the influence of pH and buffer concentration on Thermincola ferriacetica anode biofilms in MECs (Lusk et al., 2016).

4.4.2 Inhibition of methanogenesis

Different methods for methanogenesis inhibition are depicted (Table 3.5) as follows.

4.4.2.1 Inhibition by physical methods

Most of the methanogens grow at a neutral pH. Lowering the pH below 7.0 could be a solution to stop methanogenesis. Methanogens can create CH4 at moderate temperatures and reach saturation at 37°C. Under psychrophilic circumstances, methanogen development was suppressed, and nearly no CH_4 was generated at 4°C. Other electrode and electrolyte pretreatment procedures such as ultrasonication, heat shock, and air exposure have been proven to be successful in controlling methanogen in MEC.

4.4.2.2 Inhibition by chemical methods

Generally, antimicrobial agents compete with target enzymes in metabolic pathways for methane production (Chae et al., 2010). The formation of methane from H_2/CO_2 and acetate can be inhibited by halogenated hydrocarbons (such as $CHCl_3$ or CHX_3).

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TABLE 3.5 Different methods for methanogenesis inhibition.

Method	Parameter	Hpr ($m^3/m^3/d$)	Result	References
Applied voltage	0.8 V	–	Methane production increased <0.8 V	(Ding et al., 2016)
Oxygen exposure	Bioanode was exposed to air for 24 h	–	No methane was produced for 12 h	(Ajayi et al., 2010)
Rapid H_2 extraction	–	1.58 ± 0.5	No methane production	(Lu et al., 2016)
Biocathode	Biocathode at −0.65 V	10	Methane was detected at starting up	(Rozendal, Sleutels, et al., 2008)
Heat treated electrode	Bioanode at 100°C for 15 min	0.69	1% methane	(Hu et al., 2008)
Chemicals	2-bromoethanesulfonate (10 mM)	1.08 ± 0.1	No methane production	(Hari et al., 2016)
	2-bromoethanesulfonate (286 μM)	–	No methane production	(Chae et al., 2010)
	2-bromoethanesulfonate (50 mM)	–	Complete methanogen inhibition	(Parameswaran et al., 2009)
	5% chloroform	2.39 ± 0.3	No methane was produced in fed batch culture	(Zhang et al., 2016)

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4.4.3 Enhancement of biofilm

The utilization of conductive and stable materials that enhance electron transmission is critical for exoelectrogenic biofilm formation. Liu et al. (2017) investigated the effects of heat treatment on stainless steel felt utilized for the cathode in an MEC-AD. They discovered that heat treatment created 3D iron oxide nanoparticles the exterior of heat-treated stainless steel felt (HSSF), allowing for an increase in electroactive area, which aided in the formation of electroactive biofilms (Liu et al., 2017). The influence of external voltage through anode biofilm was examined by Zakaria et al. Microorganisms exposed to 0.4 V revealed a robust and balanced colony of fermentative and electroactive bacteria capable of lowering COD. Positive potentials, contrasted with, had a deleterious impact on the biofilm. The MEC anodic biofilm is dominated by *Desulfovibrio* sp., *Acidaminococcus* sp., *Desulfocapsa* sp., and *Acetobacterium* sp. (Almatouq et al., 2020). The process of free cells adhering to an electrode surface is important for biofilm formation. Functional groups on material surfaces make direct contact with the bacterial outer membrane and extracellular polymeric substance (EPS). Unstable adsorption, stable adsorption and microcolony formation, biofilm expansion and maturation, and biofilm aging and dissociation are the four processes that make up a typical biofilm.

5. Conclusion

For more than a century, hydrogen has been suggested as a practical, clean-burning fuel. Using renewable energy sources to create hydrogen could eventually replace fossil fuels, alleviating environmental, political, and resource concerns. But hydrogen is not readily available in the environment. As a result, hydrogen must be electrolyzed from water or isolated from carbon fossil fuels. Moreover, traditional manufacturing procedures have been impeded by the high cost. MECs are a promising technology for biohydrogen production by electrohydrogenesis. Microbial electrolysis is a renewable method of creating hydrogen from many types of wastewaters. But there are several bottlenecks of MEC that has become major problems in scaleup processes and limits this technology for commercial applications. Additionally, MEC is still in its developing stage, and the techniques for improving it must be thoroughly examined. This chapter summarizes biohydrogen production from biowastes using MECs, their disadvantages, and strategies to enhance the biohydrogen production by MECs. MECs play an important role to these hydrogen demands by producing huge amounts of hydrogen from renewable resources such as biomass and wastewaters. The concept of MEC is now well proven, and advancements have been made regarding to the performance in only a few years since its discovery. To discover a mature hydrogen production technology, several research questions still need to be addressed (Rozendal, Sleutels, et al., 2008): (1) more experience is needed with real organic feedstock containing complex organic substrates such as polymeric and particulate

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substances; (2) novel, more cost-effective chemical and biological cathodes need to be developed that show less potential losses and are not platinum based; (3) membrane that has pH gradients needs to be eliminated, or membranes should not be utilized in reactor; (4) methanogenic consumption of the hydrogen product required to be prevented (in case of membraneless MECs and/or MECs with a biocathode). A rapid advancement in MECs that are being helped by the growth in related MFCs, combined with additional funding and research into microbial electrolysis, should allow for rapid commercialization of this new biohydrogen technology.

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Chapter 4

Electrochemical reduction of heavy metals from industrial effluents

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Abstract

Heavy metals are the most widely used chemical catalysts for a broad spectrum of industries, including steel making, electronics, batteries, and leather tanning. These industries are exonerating this toxic heavy metal-containing wastewater as industrial effluents into the surrounding environment, which ultimately alters environmental biodiversity and influences community health. Therefore, environmental and human safeties need to be a foremost priority to procure at present. In this aspect, electrochemical reduction is one of the most efficient processes to minimize toxic heavy metal contamination in industrial effluent before it is disposed of. Environmental compatibility, higher efficacy, and higher cost-effectiveness make the electrochemical reduction process for heavy metal remediation an attractive and industrially feasible technology. Electrochemical reduction of toxic heavy metals involves distinct segments such as electrodeposition, electrosorption, electrodialysis, electrodeionization, bio-electrochemical reduction, and photoelectrochemical reduction. However, the current state of the electrochemical reduction approach has several drawbacks, including concentration polarization from dilute metal ions, dendrite and spongy deposit formation, sluggish metal ion transportation kinetics, and salvage reactions from the hydrogen development and oxygen reduction networks. To this end, the current extensive literature review deals with deep insight into the current advances in electrochemical reduction of toxic heavy metals to ameliorate the potentiality of electrochemical process performances upon heavy metal remediation and recovery from industrial effluents in the near future.

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Keywords
Community health management; Electrochemical reduction; Environmental compatibility; Heavy metal contamination; Heavy metal recovery; Industrial effluents.

1. Introduction

One of the primary reasserts of water pollutants is heavy metals and different persistent toxic substances containing industrial wastewater (Tran et al., 2017). For manufacturing product in industry, metals are used (Maarof et al., 2017). An industrial effluent contains copper, nickel, zinc, and lead (Tran et al., 2017). Health and the natural ecology are threatened by heavy metal contamination due to its toxic and nondegradable properties (Yang et al., 2021). Heavy metal recovery and recycling techniques are explained, together with the rising costs of industrial metals (Maarof et al., 2017). In addition to reducing environmental pollution, recovering heavy metals from industrial waste also serves as a reliable source of heavy metals (Yang et al., 2021). Only 8% of industrial and municipal wastewater is treated where more than 80% of the wastewater is neither collected nor handled and is launched into the surroundings without right treatment. Thus, the industrialization process has a negative impact on the environment worldwide (Devda et al., 2021). Some heavy metals recovering and eliminating methods are adsorption, chemical precipitation, biological remediation (Yang et al., 2021), ion exchange, coagulation−flocculation, and flotation (Maarof et al., 2017). Adsorption's primary drawback is its heavy reliance on certain functional groups, which raises the expense of design materials. Chemical precipitation uses a wide variety of chemical reagents, and the sludge may produce secondary pollutants. Difficulties in screening microbial populations and processing biological materials are challenges in biological remediation method (Yang et al., 2021). Ecofriendly biological method phytoremediation may involve in metal recovery. This chemical−physical treatment has a plenty of drawbacks, such as excessive operational costs, incomplete elimination, and intake of an enormous quantity of energy or requirement for huge portions of chemicals (Maarof et al., 2017). To catch up with the demand for heavy metal recovery, a cheaper, sustainable, and more energy-efficient electrochemical recovery process was developed. After an electric current is applied, metal ions migrate to the electrode surface, enriched at the electric double layer. The pure metal ions are fixed to the electrode surface, or precipitate near the surface of the electrode after a redox reaction (Hazmi et al., 2024; Tomar et al., 2023). By this method, metal ions can be recovered (Yang et al., 2021). Advantages of electrochemical technologies are ease of maintenance, no addition of chemicals, high efficiency, flexibility, little sludge, by-products (Devda et al., 2021), environmental compatibility, and versatility. The tendency to use electrochemical technology for water and wastewater treatment has increased

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significantly over the past two decades (Maarof et al., 2017). Nitrogen and phosphorus are extensively used as agricultural fertilizers. As the production of nitrogenous fertilizers is energy-consuming and phosphorus generation will run out in the next decade, recovery of nitrogen and phosphorus from wastewater is gaining popularity. After treatment, an industrial effluent contains a less number of pollutants that are less damaging for environment and human health released into the environment (Devda et al., 2021). But electrochemical process also contains some drawbacks such as high energy consumption, low conductivity of electrodes, low removal or recovery of heavy metals, especially for dilute metal ions, undesirable reactions, and poor electrode reliability (Jadhav et al., 2024). Therefore, it is obligatory to study electrochemical process more deeply to minimize the shortcomings of the existing processes (Maarof et al., 2017). The chapter provides a thorough examination of the different electrochemical recovery techniques (Yang et al., 2021) for heavy metals, with a focus on electrodeposition, electrosorption, electrodialysis, electrodeionization (Jin & Zhang, 2020), electrocoagulation, and electroflotation (Tran et al., 2017). The chapter depicts and analyzes their mechanism, effects of different factors, and recovery efficiencies. This chapter emphasizes the challenges and future opportunities of electrochemical technology in heavy metal recycling (Yang et al., 2021).

2. Source of heavy metals in industrial effluents

To meet the expectancy of today's lifestyle, maintenance industry plays a major role to fulfill it. Industries produce most of the daily essentials that are needed for our daily lifestyle. Industries supply us with the essentials, but on the other side of it, they produce waste effluents, containing heavy metals. Heavy metals do not seem to be so smart for our health, and it is also toxic to the environment (Gautam et al., 2014). Discharge of effluents from industrial complexes with no treatment contains numerous organic and inorganic pollutants that cause pollution within the environment (Agarwal & Singh, 2017). In industrial effluents, some metals such as mercury, lead, cadmium, and arsenic are the main reason of water pollution. These significant metals present in effluent release from industrial complexes, might be poisonous, and can show toxicity effects or carcinogenic activity that are a threat to human health as well as environmental health (Agarwal & Singh, 2017; Gautam et al., 2014). The heavy metals that are found in effluents are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni), and mercury (Hg) (Mitra et al., 2017). Various industries are responsible, such as textile, tannery, dye, electronics, petrochemicals, paint, food industry, etc. The heavy metal chromium is discharged from the effluent of animal skin tanning, electroplating, nuclear energy plants, and textile industries. Industries that discharge chromium as its industrial effluent, such as the textile industry, use dye to impart color and discharge a large quantity of chromium because of the

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employment of the dye. The dye contains many toxic materials, especially chromium. Other industries such as electroplating, tannery, paints, and petroleum industry also release chromium in the effluent (Mitra et al., 2017). The sources of copper in industrial effluents are electroplating, paints, fertilizers, pesticides, dyes, and petroleum refining industries. Nickels are poisonous metals released from the battery industry, electroplating industry, cosmetics industry, paint industry, dyes, and stainless steel industry as an industrial effluent. Mainly the divalent form of nickel [Ni (II)] is found in effluent (Kumar et al., 2019). Heavy metals such as mercury possess toxic properties that have a very bad effect on humans, animals, and the environment. Mercury is released from the industries such as batteries, mercury vapor lamps, thermal power plants, steel, cement, and rice mills as industrial effluents. Methyl mercury is the most toxic form of mercury in the environment. Zinc is considered toxic metals that are released from the commercial effluents of cosmetics, plastic, paints, dyes, and rubber industry (Lim et al., 2021). Table 4.1 depicts permissible limits of heavy metals and their impact on human and environment.

3. Heavy metals reduction method

3.1 Electrochemical

3.1.1 Electrogeneration of reactive oxygen species

The electrogenerated reactive O_2 species are used as water disinfectants, by removing organic pollutants from industrial effluents and inactivating microorganisms (de Oliveira Campos et al., 2018; Jeong et al., 2006). Reactive O_2 species is an electrochemical technique, based on electrochemical oxidation. Reactive O_2 species are generated by electrons in an electrochemical reaction and produce hydroxyl (OH) by oxidation of water in the anode of the chamber. One reaction is given in the following:

$$H_2O \rightarrow OH + H^+ + e^-$$

The two pathways taken for inactivating microorganisms and organic pollutant removal from effluent are direct oxidation and indirect oxidation. During the electrolysis, reactive oxidants are generated, which mediates the indirect oxidation pathway (Martínez-Huitle et al., 2015). In the direct oxidation pathway, electrons are transferred between the cells and electrode; in the cell wall, dimerization of enzyme occurs and results in lysis of the cell (Jeong et al., 2006). During the oxidation of water, some oxidants (•OH, O_3, H_2O_2, etc.) are produced and that mediates the indirect oxidation pathway. Hydroxyls (OH) are common oxidants produced from one-electron oxidation of water that inactivates microorganisms by initiating injury in the cell wall, eventually causing lysis of the cell. Other than OH ions, O_3 and H_2O_2 can cause lysis of the cell (de Oliveira Campos et al., 2018).

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TABLE 4.1 Heavy metal's permissible limits and impact in human and environment.

Sl. No.	Heavy metals	Permissible limits in industrial effluent (mg/L)	Permissible limits in drinking water (mg/L)	Heavy metals impact in human and environment	References
1.	Lead (Pb)	0.05	0.015	The upper permissible range of lead decreased reproduction and growth in animals and plants. On the other side, it causes neurological disorders and kidney malfunctioning in humans.	(Gautam et al., 2014)
2.	Zinc (Zn)	5.0	0.05	High levels of zinc present in the environment are hazardous to the environment. Zinc is an essential diet of our daily life but overconsumption of it causes skin irritation and anemia in humans.	(Oyaro et al., 2007)
3.	Copper (Cu)	3.0	0.05	Copper can affect the activity of soil by influencing the activity of microorganisms and slowing down the decomposition of organic matter in the soil. In humans, copper within permissible limits helps in bone and tissue development. The upper range of copper can cause liver and kidney failure, abdominal pain, and vomiting in humans.	(Gautam et al., 2014)
4.	Arsenic (As)	0.1	0.01	Arsenic has a great impact on the environment. It inhibits the growth of microorganisms. Long-time exposure to arsenic in food or ingesting water can provoke cancer and skin lesions.	(Dziubek, 2017)

Continued

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TABLE 4.1 Heavy metal's permissible limits and impact in human and environment.—cont'd

Sl. No.	Heavy metals	Permissible limits in industrial effluent (mg/L)	Permissible limits in drinking water (mg/L)	Heavy metals impact in human and environment	References
5.	Cadmium (Cd)	0.01	0.005	Cadmium is a toxic heavy metal, which prevents the growth of plants, animals, and microorganisms. Cadmium is a carcinogenic metal to humans. It causes cancer and also damages the lungs and reproductive system in the human body.	(Agoro et al., 2020)
6.	Chromium (Cr)	0.5	0.05	As chromium is a toxic metal, it harms plant metabolic activity. It reduces crop growth and crop yield. It has a carcinogenic activity in the human body. It causes bone demineralization and renal dysfunction in humans.	(Pradhan et al., 2017; Prasad et al., 2021)
7.	Nickel (Ni)	2	0.1	A major environmental problem associated with nickel is the emission of greenhouse gases, microorganism habitat destruction, etc. Acute ingestion of nickel with water causes shortness of breath, vomiting, and diarrhea in humans.	(Mahmud et al., 2016)
8.	Mercury (Hg)	0.05	0.002	Mercury is a persistent, bioaccumulative, toxic pollutant. It accumulates in water, converts into toxic form, and enters the food chain. It causes neurological disorders by affecting the central nervous system. It also affects liver and kidney in humans.	(Kinuthia et al., 2020)

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3.1.2 Electrogeneration of chlorine active species

Chlorine energetic species is an electrochemical technique that involves water disinfection. Chlorine energetic species are generated by electron transfer in the anode. Active chlorine species such as HClO and ClO increase oxidation and remove organic pollutants in industrial effluents. Chlorine is often found in natural water and industrial effluents that make an imminent presence of energetic chlorine species that helps in oxidation. The presence of chloride in electrochemical reaction favors the production of chlorine, hypochlorous acid, and/or hypochlorite. The electrochemical reaction chamber's anode is where the oxidation of natural pollutants and chloride ions takes place. The medium or reactor's pH scale has a significant impact on the oxidation of chlorine (Chung et al., 2018; Hand & Cusick, 2021).

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{4.1}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{4.2}$$

$$HClO \leftrightarrow H^+ + ClO^- \tag{4.3}$$

The aforementioned equations briefly describe the oxidation of chlorine. The oxidation process depends on the chemical composition and structure of the electrode. Hypochlorous acid is the product of chloride oxidation; it is a weak acid (pKa) that creates equilibrium with hypochlorite (de Oliveira Campos et al., 2018; Martínez-Huitle et al., 2015).

$$\text{Organics} + ClO^- \rightarrow \text{intermediates} \rightarrow Co_2 + Cl^- + H_2O \tag{4.4}$$

Eq. (4.4) shows that active chlorine species oxidize natural pollutants in an exceedingly homogenized liquid phase. This indicates that a crucial function also can be achieved via way of means of floor electrochemical reactions. The reaction of organics by electrogenerated active chlorine is stricken by many factors as well as the sort of electrochemical reactor, the character of the anode, the temperature, the pH, the applied current or potential, the flow rate and the fluid dynamics, the concentration of chlorides, and the nature and concentration of organic pollutants (Martínez-Huitle et al., 2015).

3.2 Physiochemical

Physicochemical processes are used to treat wastewater in the past as a primary treatment. Some major disadvantages such as sludge generation, being incapable of large-scale treatment, expensive chemicals requirement, and high energy consumption are those factors that limit physiochemical treatment to be applied in industrial effluent treatment (Nur Hazirah et al., 2014). The physicochemical process includes chemical precipitation, adsorption, membrane separation, filtrations, sedimentation, flotation, etc. (Bhargava, 2016). In this context, chemical precipitation, adsorption, and membrane separation are depicted in details.

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3.2.1 Chemical precipitation

Chemical precipitation is employed to get rid of dissolved metals from industrial effluent. This process converts dissolved metals to an insoluble complex by a certain chemical, reacting to the soluble metal and precipitating it. The precipitate (i.e., insoluble complex) is separated by filtration technique (Bhargava, 2016).

3.2.2 Adsorption

This physiochemical process is employed to eliminate a certain compound from industrial effluent, by adsorption into the solid surface. It is mainly the interface between solid and liquid phases. The toxic metals are adsorbable into the solid surface either by van der Waals interaction (physical) or by covalent bonds (chemical) (Nur Hazirah et al., 2014).

3.2.3 Membrane separation

Similar to adsorption, which eliminates pollutants from wastewater, membrane separation is an interface between solid and liquid phases; however, it was created to address certain problems that adsorption causes. In this technique, the solute is separated by hydrophobic interaction between membrane and solute. Processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are developed mechanisms from the membrane separation technique (Nqombolo et al., 2018).

4. Mechanism of electrochemical reactors

To neutralize the charge of particles, an electrode is used to supply ions in wastewater. It leads to the initiation of the coagulation process. Undesirable contaminants can be removed by this process. An electrolytic reaction occurs at the surface of each electrode (Tran et al., 2017). On the positive side, or anode, oxidation occurs. The reduction process occurs in the cathode (Qasem et al., 2021). In an anode, metal n+ is produced from metal (Tran et al., 2017). The cathode or negative side receives electrons from the anode (Qasem et al., 2021). At the cathode, water dissociates to form OH− and H_2. OH− and metal n+ produce metal−(OH)n as a precipitate (Tran et al., 2017). The reaction in the anode and cathode together called redox or reduction−oxidation reaction (Qasem et al., 2021).

$$\text{At anode: Metal} = \text{Metal } n^{+} + ne^{-}$$

$$\text{At cathode: } nH_2O + ne = nH_2{}^{+}\ (g) + OH^{-}$$

$$\text{Overall: Metal} + nH_2O + OH- = \text{Metal-(OH)n (s)} + nH_2\ (g)\ \text{(Tran et al., 2017)}$$

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Flocs are formed by aggregation of destabilized particles. In cathode, hydrogen bubbles are generated, which induce the flotation of most sludge. Cathode material has excellent surface area. Metal hydroxide precipitates on cathode surface. Insoluble contaminants attach to generated gas bubbles (Tran et al., 2017). Anode can be arranged in different ways, for example, monopolar electrodes in series (MP-S) arrangement, monopolar electrodes in parallel (MP-P) association, and bipolar electrodes in series (BP-S) arrangement. Different types of the electrochemical method are decided by the type of anode and cathode. It also influences the removal efficiency of specific metal ions. Electrochemical processes are mainly classified into ER, EC, EF, and EO processes (Qasem et al., 2021). In ER, or electrodeposition, targeted atoms are deposited over the top surface of the cathode. No sludge is formed (Yang et al., 2018). The performance of the wastewater treatment is affected by reactor design and the operating conditions (Jin et al., 2020). In EC or electrocoagulation method, diffusion cations of anodic metal, hydroxy complex generation (coagulants), aggregate firmness and phase partition, and construction and flotation are the mechanisms. EC uses nontoxic steel (iron) or aluminum electrodes (Moussa et al., 2017). Using AC instead of DC can reduce power consumption and increase removal efficiency (Liu et al., 2020). The mechanism of EF or electroflotation method is to electrolyze water on insoluble electrodes and introduce flotation to promote the treatment process. Being insoluble and noncorrosive and having excessive catalytic activity, reactions with Cl_2 and O_2 in the electrolyte are achieved in Ti-based anodes (Chen et al., 2002a,b). Sometimes EF and EC are hybridized to improve the performance of the system (Mazumder et al., 2020). EO or electrooxidation process is divided into direct and indirect process. NaCl concentration affects the performance of the indirect oxidation by chlorine. This process is independent on current intensity (Ammar et al., 2016). In the anode surface, pollutants exchange electron and form polymeric layer in surface. It leads to electrode deactivation and degrading efficiency. As anode Pt, Au, Mn, boron-doped diamond (PbO_2), and mixed metal oxide (MMO) are used (Martínez-Huitle & Ferro, 2006). The treatment performance is suffering from the presence of various sorts of metallic ions in wastewater (Qasem et al., 2021).

5. Electrochemical metal recovery techniques

Different electrochemical techniques are used to remove heavy metals from industrial effluents (Maarof et al., 2017). Table 4.2 contains some electrochemical techniques to remove heavy metals with their removal efficiency and application.

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TABLE 4.2 Electrochemical metal recovery techniques applications and recovery efficiency.

Sl. No.	Technique name	Metals recovered	Recovery efficiency	Application	References
1.	Electrodeposition	Cu	98%	Eliminates heavy metal from industrial effluent, recovers some precious metal (I.E. silver, gold, platinum) from wastewater treatment. It makes potable water from contaminated water, treated water can also be used in agricultural field.	(Kuleyin & Uysal, 2020; Liu, Sun, et al., 2019; Liu, Wu, et al., 2019)
		Cd	97.3%		
		Pb	98.5%		
2.	Electrosorption	Cr(VI)	94%	Heavy metals are efficiently eliminated by this technique. It is highly efficient in removal of ions. It recovers some products such as salt ions, metals. It is applicable in making water/brackish water into consumable water.	(Chen et al., 2020; Li et al., 2018; Zhao et al., 2018)
		Pb,Cd(II)	97%		
		Cu(II)	90.5%		
		As(V)	98.8%		
		Ni (II)	88.90%		
3.	Electrodialysis	Li(I)	91.26%,	Removes dissolved ionic substances from water, recovers drinking water. It can be used in operations of concentration, dilution, desalination, regeneration, treat wastewater and recover water. It can recover other products heavy metal ions, salts, acids/bases, nutrients, and organics, or electrical energy.	(Casqueira et al., 2006; Gurreri et al., 2020; Jin & Zhang, 2020; Maarof et al., 2017; Oliveira Da Mota et al., 2015).
		Fe(II), Fe(III), Na(I),	97.8%		
		Phosphorus	50%		
		Cu	93%		
		Cr	95%		
		As	99%		

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4.	Electrodeionization	Li(I),	90%	Removes and recovers ions from water, removes toxic chemicals, radioactive pollutants, heavy metal ions and corrosive anions; and regenerate valuable metals, use in deionization of water and the removal of nitrates.	(Arar et al., 2014; Jin & Zhang, 2020; Kim et al., 2017; Rathi & Kumar, 2020).
		Cr(VI),	99%		
		As,	100%		
		Cr(III), Cr(V),	99%		
		Cu(II),	93.2%		
		Ni	89.5%		
		Pd	99%		
5.	Electrocoagulation	Ni^{2+}	98%	Ease of sludge dewatering and setting heavy metals discharge from various anthropogenic sources and industries are challenging to treat as they are toxic and nonbiodegradable. EC technique examines to eliminate the most toxic and abundant heavy metals existed in wastewater. EC process is an effective treatment technique for heavy metals elimination, those are difficult to eliminate by other conventional techniques.	(Bazrafshan et al., 2015; Shahedi et al., 2020)
		Cu^{2+}	99%		
		Cr	100%		
		Ni^{2+}, Zn^{2+}	100%		
6.	Electroflotation	Zn	96%	Removes suspended particles from water using gas bubbles generated during electrolysis of water, treat wastewater from industrial effluents, removes hydrophobic ions from water.	(Kyzas & Matis, 2016; Mohtashami & Shang, 2019).
		Cu	99%		
		Pb, Ba, Zn	97%		
7.	Electro-oxidation	Cu^{2+}	100%	Reduce color and chemical oxygen demand in distillery wastewater by using electrooxidation process.	(Shiying et al., 2009; Piya-Areetham et al., 2006; Wang et al., 2022)
		CN^{-}	100%		

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5.1 Electrodeposition

Electrodeposition (Fig. 4.1A) is an aged technique invented by Luigi Brugnatelli in 1805, which removes metals from metal-contaminated water. This technique is also called as electroplating technique. Nowadays, this method is employed within the removal or recovery of significant metals from industrial effluent to prevent environmental pollution and to isolate some precious metals (silver, gold, platinum) from it (Maarof et al., 2017). The principle behind the electrodeposition technique is that after introduction of electrolyte solution, metal ions are converted into solid metal and deposited upon the porous cathode surface when a sufficient amount of electric current passes through the electrolyte solution. Mainly electrolytes are the metal ions contained in the aqueous solution. In this technique, the anode is immersed in the solution, and oxidation takes place in the anode. The cathode is placed above the anode where reduction takes place and high purity metal is deposited into the porous cathode (Kuleyin & Uysal, 2020; Maarof et al., 2017). It is an electrochemical reaction. The following equation suggests the electrochemical reaction in the cathode and anode of the electrodeposition technique.

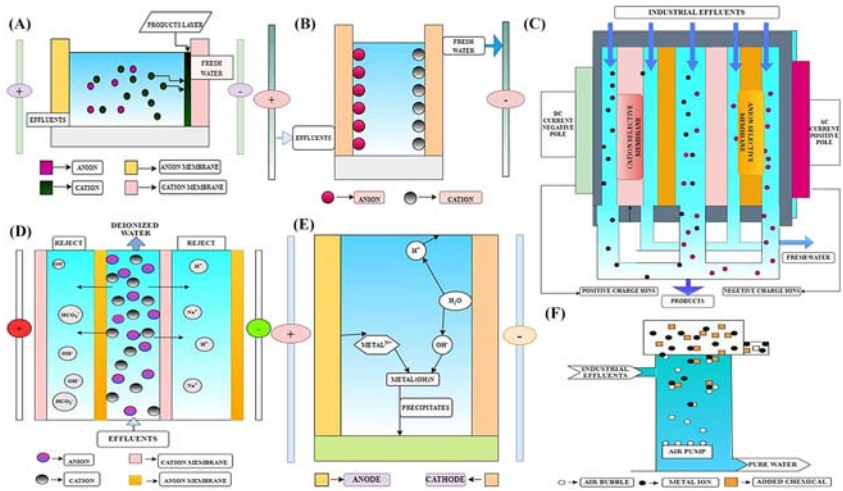

FIGURE 4.1 Different electrochemical techniqueto reduce Heavy Metals from Industrial Effluents. (A) Electrodeposition: Electrodeposition removes metals from metal-contaminated water; (B) Electrosorption: The electrosorption or CDI technology removes ionic/heavy metal contamination from effluent using an applied electric field; (C) Electrodialysis: Electrodialysis uses an ion exchange membrane to transport aqueous ions, separating concentrated and dilute solutions through electrostatic interaction within the membrane; (D) Electrodeionization: Electrodeionization uses a charged membrane to separate cations and anions, making it valuable for water purification and desalination; (E) Electrocoagulation: Electrocoagulation The metal anode in electrocoagulation oxidizes to form metal ions (Al^{3+} and Fe^{2+}), which react chemically to produce metal hydroxide; (F) Electroflotation: Electroflotation generates hydrogen and oxygen bubbles through water electrolysis, enhancing the buoyancy of small solid particles.

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Cathodic reaction

$$M^{+}(aq) + 2e^{-} \rightarrow M^{0}(s) \quad (4.5)$$

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \quad (4.6)$$

Anodic reaction …

$$4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O + 4e^{-} \quad (4.7)$$

From the study of Kuleyin and Uysal, on recovery of copper from industrial effluent, it shows that effects of certain parameters such as an electric current, pH, conductivity, and initial copper concentration influence the copper deposition. An increase in current value will increase the copper removal efficiency. The pH 3 is the optimum value for copper removal by electrodeposition (Kuleyin & Uysal, 2020). From the aforementioned study, it is indicated that the effect of current (voltage), pH, and conductivity influence the electrodeposition process. Under optimum conditions, it achieves high metal recovery efficiency. The electrodeposition technique has several advantages to perform because no chemical reagent is required to carry out this process, no sludge is produced in the electrodeposition technique, and it is cost-efficient and highly selective on metal ions. These parameters favor the electrodeposition process (Chen & Lim, 2005).

5.2 Electrosorption

Electrosorption (Fig. 4.1B) process is based on capacitive deionization (CDI) technology. It includes the employment of electrochemical and adsorption/desorption processes in electrosorption (Li et al., 2017). CDI technology is also known as electrosorption at salt ions or electrochemical demineralization (Hu et al., 2015). Electrosorption or CDI technology is employed within the treatment of waste matter to get rid of serious metals from water and to form potable water from saltwater or brackish water (Maarof et al., 2017). The electrosorption or CDI technology separates ionic/heavy metal contamination from effluent by using a double-layer electric bed under an applied electric field; the heavy metal contamination moves toward the positively charged electrode. Then electric double layer is further adsorbing the heavy metals, and the potable water or heavy metal-free water generation has been possible. Under applied electric field, this process is carried out when an electric field is removed, the absorbed metals are moved back to the affluent, and the electrode is regenerated by desorption. The voltage used in CDI technology is 0.6−2.0 V; it is required to suppress metal electrodeposition (Liu, Wu, et al., 2019; Liu, Sun, et al., 2019; Wang et al., 2019). For development in electrosorption, an ion exchange membrane is introduced into capacitive deionization for increasing metal recovery efficiency. The induction of ion exchange membrane into capacitive deionization is called membrane capacitive

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deionization (MCDI). A straightforward flush of counterions from the conductor region during the ion unleash stage is another benefit of MCDI that makes it easier for electrosorption to occur during subsequent cycles (Lee et al., 2014; Porada et al., 2013).

5.3 Electrodialysis

Electrodialysis (Fig. 4.1C) or ED is electricity-driven membrane separation process used in heavy metal elimination of industrial effluents. In this process, an ion exchange membrane is used to transport aqueous ions. Ions are transferred due to electrostatic interaction within the membrane (Ibrahim Al-Karawi, 2010). It separates concentrated and dilute solution in two compartments. Permeability of the ion exchange membrane, charge/mobility/relative concentrations of ions, and applied voltage/current determine the direction of ion transport. Enhancement of specific ions is provided by selective transport and retention of the membrane (Jin & Zhang, 2020). 95% pure lithium salt can be produced by ED with high removal efficiency rate ($\sim$80%). In this process, the product can be acquired by simple precipitation (Gmar et al., 2019; Song et al., 2018). Electrodialysis is used with EDI and ion exchange to extract radioactive element (Jin & Zhang, 2020). Electrodialysis is used in medical, food, chemical, and metallurgical industries for purification by means of desalination. At first, for desalination and concentration of seawater, electrodialysis was developed (Chaudary et al., 2000). Recently, it is used in heavy metals removal from industrial effluents. Energy expenditure in electrodialysis links with the quantity of electrolytes to be extracted and not to the volume of water to be treated (Ibrahim Al-Karawi, 2010). Nitric acid and sodium hydroxide are recovered from industrial wastewater by electrodialysis, using ion-perm selective membranes containing $NaNO_3$. Copper can be recovered by electrodialysis in cathode compartment with low operation cost. It reduced water pH from 9 to 6.5−7.5. Thus, there is no need of adjusting pH before discharging water into waste streams (Cherif et al., 1997). 99.9% of Cr(VI) with 4 mg/L concentration were recovered from rinse water from chromating bath by electrodialysis. The remaining water can be reused as rinse water (Ibrahim Al-Karawi, 2010). 93% of Cu, 95% of Cr, and 99% of As were recovered by chromated copper arsenate timber waste using electrodialysis cell (Ribeiro et al., 2000).

5.4 Electrodeionization

Electrodeionization (EDI) (Fig. 4.1D) or capacitive deionization (CDI) (Chen et al., 2020) and membrane capacitive deionization or MCDI are electrically driven membrane processes (El Batouti et al., 2021). EDI can be utilized in water purification and desalination, and it does not cause secondary pollution (Jin & Zhang, 2020). It uses a charged membrane to separate cation and anion,

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either a cation exchange membrane or an anion exchange membrane. Electrical potential differences produced by this process are utilized as the driving force of ion transport. Electrodialysis's removal efficiency decreases as ion concentration decreases. To resolve this problem, EDI was created, which is a combination of ED and conventional ion exchange processes (Chen et al., 2020). To pursue radioactive element removal, a symbiotic integration between EDI technology and ion exchange was built in 1955 (Jin & Zhang, 2020). At low ion concentration, dilute compartment's conductivity is maintained by the existence of ion exchange resins or ionic bridge. Two streams with varying ion concentrations are produced by EDI, which allow purification and concentrating applications. The best effluent quality is produced by ion exchange resins with EDI in a dilute compartment. EDI is affected by initial concentration, flow rate, and sulfuric acid (Chen et al., 2020), permselectivity of the ion exchange membrane, charge/mobility/relative concentrations of ions, and applied voltage/current (Jin & Zhang, 2020). 50−1583 mg/L Ni can be recovered by EDI with a 31.7 concentration factor and a 40% current efficiency (Lu et al., 2010). MCD is CDI with incorporated ion exchange membranes (IEMs) in the forepart of electrodes (Chen et al., 2020). MCDI uses adsorption and desorption processes. In adsorption, ions are attracted to an electrode by electrostatic force, and it is affected by electrode's ionic capacity. In the adsorption process, freshwater or desalinated water is produced. After electrodes reach saturation, regeneration occurs in which the polarity of electrode is reversed. Effluent with a high ion concentration is generated by desorption process (Al-Marzooqi et al., 2014). However, 07−99.94% elimination along with 1.42−1.52 of Pd selectivity toward ammonium ions can be obtained by MCDI (Kim et al., 2017). MCDI consumes less energy than electrodialysis (Jin & Zhang, 2020). Hybrid capacitive deionization (HCDI) includes Faraday electrodes containing inorganic intercalation compounds and electric double-layer carbon electrodes. This provides high ion removal capability, fast ion capture, and excellent durability (Li et al., 2019). Membrane-free electrodeionization (MFEDI) was developed to eliminate the membrane fouling, scaling, and concentration polarization issues (Shen et al., 2015). Zn and Cu can be obtained from water by membrane CDI with AC fiber electrodes. Three chambers (an anode chamber, a cathode chamber, and a concentrated chamber located between them) are involved in this process. In anode and cathode chamber, $CuSO_4$ gets absorbed, and in concentrated chamber, it gets enriched. For water purification and resource recovery, this system is used (Jin & Zhang, 2020).

5.5 Electrocoagulation

The coagulation process defines as a method to alter the physical state of colloids by adding a coagulant into the wastewater (Verma et al., 2012). The colloids will be able to adhere one another to form larger agglomerates.

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The coagulant is normally an inorganic metal salt, such as iron or aluminum salt that is added to wastewater to facilitate the coagulation process. The coagulant dissociates into positively charged ions upon contact with water added to neutralize negatively charge surface of the colloidal particles. Once the surface charge neutralizes, the fine particles become unstable and are capable of sticking together to form larger groups of particles. An indirect approach of another electrochemical process is known as electrocoagulation (Fig. 4.1E). The anode is normally aluminum or iron (de Mello Ferreira et al., 2013; Eiband et al., 2014). Iron performs better compared with aluminum for the removal of heavy metals (Mouedhen et al., 2009). For the removal of chromium compared with iron and aluminum, copper is the best anode (Mella et al., 2015). The metal anode, which is chosen, oxidizes to form metal ions (A^{l3+} and F^{e2+}) upon the application of a current and, upon chemical reaction, forms a metal hydroxide series. This metal hydroxide behaves as a coagulant to destabilize the metal contaminants that are present in electrolyte, in an appropriate condition, causing them to agglomerates into larger particles (Prica et al., 2015). This kind of proposal removes metal ions from wastewater by transforming the soluble metal into its insoluble hydroxide form. The pollutants eliminate either by chemical reaction and precipitation or by initiating the colloid to coalesce and further float in the reactor (Sahu et al., 2014). Electrocoagulation generates less sludge (Mansoorian et al., 2014) and offers cheaper operational cost of chemical consumption compared with the chemical coagulation process. Electrocoagulation is an electrochemical approach that uses an electrical current to remove metals from solution. It is also effective in removing suspended solids, tannins, dyes, and dissolved metals (Rincon et al., 2014). The study of this process mainly focuses on the operating conditions such as the initial concentration, treatment time, current density, and electrode gaps. This process bases on the continuous in situ production of a coagulant in the contaminated water. This technique does not require supplementary addition of chemicals and reduces the volume of produced sludge (Bazrafshan et al., 2012). To this end, EC files an application for wastewater treatment at the turn of the 19th century (Matteson et al., 1995).

5.6 Electroflotation

Electroflotation (Fig. 4.1F) is a simple process to remove heavy metals (Oliveira da Mota et al., 2015). Floatation produces tiny gas bubbles of hydrogen and oxygen from water electrolysis that adheres to the solid particles, which increase the buoyancy of small solid particles (Maarof et al., 2017). Hydrophobicity is the key of floatability (Oliveira da Mota et al., 2015). Pollutant disposal efficiency and the power and/or chemical consumptions reflect the performance of electroflotation. The pollutant removal efficiency depends on bubbles size. Power consumption depends on cell design, electrode material, current density, water conductivity, etc. (Ibrahim Al-Karawi, 2010).

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Size of the bubbles is dependent on water pH; in neutral pH, there is small hydrogen bubble. Cathode materials and anode materials also affect the size of bubbles. Current density can influence gas bubbles. Particle size depends on surface condition, like finest bubbles are produced by polished mirror surface (Jim'enez, et al., 2010). The number of gas bubbles obtainable per second per unit across selective area of the flotation cell is called bubble flux. Bubble flux influences recovery of various sized particles (Wills & Finch, 2016). In an electrode system, only the upper cathode faces the wastewater flow. Bottom anode does not interact with the flow directly. So the oxygen bubbles produced by anode cannot disperse easily and form large bubbles, which decreases the availability of small bubbles and affects the flotation efficiency. High flotation efficiency is ensured when anode and cathode are in leveled position and form bubbles that can be dispersed into wastewater rapidly (Ibrahim Al-Karawi, 2010). Oliveira da Mota et al. (2015) reported that 97% of heavy metals (Pb, Ba, and Zn) were removed by electroflotation process in 20 min of operation time. In this process, a molar ratio of 3:1 for the ionic collector to heavy metals and 0.1% of bubbly agent (ethanol) was used (Oliveira da Mota et al., 2015). ECF process removes 96% of zinc (Casqueira et al., 2006) and 99% of copper (Adamovic et al., 2016). By ECF process, kaolin, silica, chalcopyrite, and sphalerite can be recovered (Sarkar et al., 2010).

5.7 Electrooxidation

Electrochemical technique is a process consisting electrodissolution of a metal at anode and production of hydrogen and hydroxide ions at the cathode. Some physical and chemical phenomena including anodic oxidation, cathodic reduction, coagulation, electrophoretic migration, and adsorption occur in an electrochemical process. The studies on electrooxidation for wastewater treatment go back to the 19th century. Since the late 1970s the extensive investigation of this technology has commenced. During the past two decades, research tasks focuses on the efficiency in oxidizing numerous pollutants on distinct electrodes (Kuhn, 1971a,b). Electrooxidation divides into two processes.

5.7.1 Indirect electrooxidation processes

Electrooxidation pollutants fulfill in contrasting ways. Use of chlorine and hypochlorite generated anodically to demolish pollutants is well known. Typically larger than 3 g/L, at high chloride concentration, this procedure can effectively oxidize many inorganic and organic pollutants at high chloride concentration. In the raw wastewater if the chloride content is low, to increase the process, a large amount of salt must be added (Kuhn, 1971a,b). Another kind of electrooxidation, mediated electrooxidation, is used in treating mixed and hazardous wastes. Metal ions, which are usually known as mediators,

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oxidize on an anode from a stable low valence state to a reactive high valence state that in turn attacks organic pollutants directly. Mediated electrooxidation usually needs to operate in highly acidic media (Farmer et al., 1992).

5.7.2 Direct anodic oxidation

By generating chemisorbed "active oxygen" or physically adsorbed "active oxygen," electrooxidation of pollutants can also occur directly on anodes. This is usually known as direct oxidation or anodic oxidation. The anodic oxidation does not need to add a huge amount of chemicals to wastewater or feed oxygen to cathodes, with no tendency of producing secondary pollution and the fewer accessories that are required. These advantages make anodic oxidation more attractive than other electrooxidation processes (Comninellis, 1994).

6. Production of by-products by bioelectrochemical and photoelectrochemical recovery

6.1 Bioelectrochemical recovery

Bioelectrochemical technology also called bioelectrochemical system (BES) is employed to knock out and recover metals from industrial effluents. This technique uses microorganisms, which are capable of converting chemical energy into electric current and other chemicals as by-products (Wang & Ren, 2014). Recently, BES is applied in treatment of effluents and recovery due to its flexibility in the operation process with cost efficiency and no chemical reagent required saving aeration energy and sludge disposal. The bio-electrochemical system (BES) is highly focused on metal recovery, mainly BES consists of an anode, cathode, membrane, microbial fuel cells (MFCs), and microbial electrolysis cells. BES is mainly divided into two parts: (1) MFCs are used for metal recovery and do not require any external energy source, because they are capable of producing it, and (2) microbial electrolyte cells (MECs) are used for metal recovery where the external energy source required to deposit the recovery metal into the external energy is provided from outside by applying electrical current (Ho & Babel, 2021). In BES, anode and cathode are separated by a membrane (i.e., ion exchange membrane). As the name suggests, the bioelectrochemical system has the same working mechanism like electrochemical: in the anode, oxidation of effluent takes place and metal is deposited into the cathode by applied electric current from outside, and in the cathode, reduction occurs. Furthermore, bio indicates that when microorganisms (MFC) are employed in a system that generates electricity, external current supply is not necessary for the transfer of metallic ions into the cathode. In the case of MECs, the energy is required from outside because MECs cannot generate electric current (Ho & Babel, 2021) (Wang & Ren, 2014). The by-product generated in BES is metal that is recovered and deposited into the cathode and electric current produced by MFCs. In BES,

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anodic chamber microorganisms are introduced to carry out oxidation, and metals are coated in cathode for recovery and removal of metal from industrial effluent (Huggins et al., 2013).

6.2 Photoelectrochemical recovery

The photoelectrochemical technique is a combination of electrochemical and photochemical processes. This is a recently developed technique in wastewater remedy for the elimination and recuperation of metals in water (Divyapriya et al., 2021; Jin et al., 2020). Photoelectrochemical approaches are composed of photoanode and cathode. Photocathode carries out oxidation: in the presence of light, it produces an electric current that transfers electron/metallic ions to recover metals from effluent deposited into the cathode (Yu et al., 2020). Here, photoanodes coated with TiO_2 metals are capable of splitting water and producing an outsized quantity of H_2 as a by-product (Jin et al., 2020). The metal electrodeposition occurs in cathode coated with carbon, Cu, or Ti plates (Wang et al., 2017).

7. Electrochemical process modeling and simulation

Modeling is the development of a mathematical description of a physical system. To narrate and foretell an electrochemical process, modeling is used. In the modeling of an electrochemical process, different viewpoints and strategies are used. Experimental studies are conducted to check the validity of a suggested model (Maarof et al., 2017). To foretell the electrolytic voltage of the electrocoagulation process, the formula has been set forward using three parameters: electrode spacing, current density, and conductivity of the solution in the cell, and validity of this equation was analyzed with experimental works. Common computational techniques (e.g., MATLAB, Math-Works, United States) are used to deduce this equation for simple theoretical analysis (Chen et al., 2002a,b). Finite element method (FEM) is used by many researchers; it subdivides a particular system into smaller parts, known as finite element (Körbahti, 2014). To solve and analyze problems of fluid flows aided by moderate or complicated computer resources, process modeling and simulation were combined with computational fluid dynamics (CFD). It has improved operational controls and serves as cost-effective tools for system scale-up purposes (Mandin et al., 2006). Until now, modeling and simulation of electrochemical processes range from laminar to turbulent flow, from static electrode to rotating electrode, from plane geometry to cylindrical/tubular geometry and from primary current to tertiary current distribution. Use of rapid emergence of computational technologies and the development of advanced simulators is very helpful in electrochemical process. An advantageous process, COMSOL Multiphysics (COMSOL, Inc., MA, United States), provided a specific module for electrochemical modeling (Maarof et al., 2017).

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Modeling and simulation for electrochemical process involved in deletion and recovery of heavy metal were conducted with experimental studies in electrorefining (Najminoori et al., 2015). To simulate the electrochemical process through hydrodynamics and mass transport models under a turbulent conditions, Rivero and coworkers proposed turbulence model coupled with Reynolds-averaged Navier−Stokes (RANS) equation in which the turbulent viscosity was derived according to the standard k-ε turbulent equation describes hydrodynamics behavior. Rivero used Butler-Volmer kinetics to describe the metal reduction, the simplified Tafel equation for water oxidation, and the electrical continuity equation for ohmic potential drop through the electrolyte. They found that COMSOL Multiphysics simulation using FEM can predict the mass transfer coefficient and the current-potential behavior for copper recovery (Rivero et al., 2015). Several researchers also worked on CFD model. Continuity equation, momentum equation (Navier−Stokes) with including buoyancy force, and steady-state transport equation for copper mass concentration were used by Hemmati et al. (2013) and Leahy and Phillip Schwarz (2011) to optimize the function of a copper refining cell. Various strategies can be utilized in modeling and simulation. Presence of multiions should be considered in modeling process. An important complementary methodology can be achieved to the theoretical and experimental approaches by electrochemical process modeling and simulation (Maarof et al., 2017).

8. Scope of electrochemical industries

Electrochemistry classically defines as the science of the chemical changes that are caused by the electric current electric current and the production of electricity from the energy of chemical reactions (Mantell, 1960). Parts and aspects of electrical engineering and metallurgy grafts by the electrochemical engineering are a branch of chemical engineering. Electrochemical engineering concerns itself, not only with all the topics generally considered as electrochemical, also with entire furnishing of power to the industries, utilization of that power, construction, the design and operation of the equipment machinery and plants, the economic considerations in the competition of electrochemical and chemical methods for the same or similar products, as well as their distribution and consumption (Kuhn, 1971a,b). Electrochemical industries are divided into the following:

- The combined electrolyte group is represented by aluminum, magnesium, and the alkali metals.
- Those industries in which the primary interest concerns with the electric current effecting reactions in the gaseous phase.
- The electro furnace ferroalloy and special alloys.
- The electrothermal group, examples of which are calcium carbide, graphite, cyanamid, and the synthetic abrasives.

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- The batteries group, of the primary and secondary type, as well as corrosion and the stability of structures and systems.
- Those of an electrolytic nature, further subdivided into those of
  - the electrodeposition type, as electroplating and electroforming;
  - the electrowinning type, as represented by the copper or zinc industries in which ore leaches;
  - the electroseparation type, represented by chlorine and alkali;
  - the electorefining group, of which electrolytic nickel or copper are examples;
  - a section that, as the result of oxidation or reduction, concerns chlorites, metallic oxides, peroxides as well as organic materials (Mantell, 1960).

Increasing use of electrochemical processes expects as electrochemical techniques become better and more widely understood and as the economics of electrochemical processing improve through use of larger and more efficient cells (Pickett, 1979).

9. Treatment of industrial effluents

- **Textile dying effluents:** Textile industry causes huge volumes of dye wastewater effluents from the constructing process that contains organic dyes and other organic/inorganic pollutants. More than 7×10^5 (Robinson et al., 2001) tons of organic dyes are manufactured by the dye industry yearly with approximately 2.8×10^5 tons/year (Jin et al., 2007) discharged directly as dye wastewater effluents after utilized in the manufacturing process. Around 40% of annual production becomes a pollution problem (de Aragao Umbuzeiro et al., 2005). The dyes that are organic in nature are hardly removed by conventional wastewater treatment technologies, such as physicochemical and biological processes (Brillas et al., 2015). The textile dye effluents attending a chemical oxygen demand (COD) range from 250 mg/L up to 1400 mg/L of O_2 (Wang et al., 2009). The EO conducts without the further incorporation of salts that act as supporting electrolyte, due to their high conductivity. The potential refinement in the removal percentage of COD or liquefied organic carbon (DOC) and color removal kinetics is firmly dependent on the initial concentration of chlorine in the treated effluents (Chatzisymeon et al., 2006). The estimated power consumption is heavily influenced by the effluent conductivity, present density, and anode material. The active anodes absorb a lower energy requirement of ca. 5.0 kWh/m^3 (Basha et al., 2012) but with underneath performances in COD and DOC removal, while nonactive anodes such as boron-doped diamond attain higher COD and DOC abatements in a shorter functioning time and energy consumption ranges in between 16 and 100 kWh/m^3. The final engineering resolution is a compromise solution in between water disposal requirements and treatment cost require. The

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decolourized water reuses in new pigmenting process after the EO treatment (Sala et al., 2014).

- **Paper industry effluents:** One of the largest manufacturing users of water is the pulp and paper mill industry with water consumption as high as 60 m^3/ton of paper produce, even with the most efficient processing methods (Thompson et al., 2001). As a result, huge volume of wastewater is represented by a very high pollutant stuffing generation. On the top of the traditional primary and secondary treatments, these effluents acutely require advance treatment processes and a step recovering of water. Due to the presence of unmanageable substances, the generated effluents frequently have a high COD, low biodegradability, and more than 200−300 various biotics with nearly 700 inorganic compounds. Such matters include absorbable organic halides (AOX), phenolic compounds, coloring compounds, additives, solvents, etc. The distribution of such species largely confides on the applied pulping and papermaking procedure (Karrasch et al., 2006). Due to incomplete demolition of toxic chemicals, the final water release can still pose high risk of environmental contagion. Recent works aim to overcome such constraints of currently acquired wastewater treatments acceptable for pulp and paper mill industries by enlarging cost-beneficial techniques for complementing or even restore some of the old therapy schemes (Kamali et al., 2015). One of the most fascinating and effective processes for treating some pollutants in wastewater that are the electrochemical process because of its convenience and greater effectiveness than other traditional and arising nonelectrochemical techniques. Two electrochemical methods that are gaining interest as a viable treatment of paper mill and pulp wastewater are EO and EC (Szpyrkowicz et al., 2005; Khansorthong et al., 2009).
- **Tannery effluent:** The tanning industry is one of the most contaminating parts of the industrial sector by generating wastewater holding an enormous load of organic and inorganic substances. The wastewater is known to contain numerous chemicals such as sodium sulfite, chromium sulfate, wetting agents, bactericides, soda ash, sodium sulfide, ammonium chloride, sodium chloride, sulfuric acid, formic acid, tannins, dyes, enzymes, resins, pigments, binder, waxes, lacquers, formaldehyde, and different types of solvents and additives (Vijayalakshmi et al., 2011). Discharge of such effluent is injurious to the nearby ecosystems due to its excessive COD and toxic potential, and eject of such effluent is noxious to the nearby ecosystems. The utter number of substances present produces the effluent a very complicated pollutant matrix that conventional biological procedure is not able to oxidize completely, particularly the tannins and ammonia the prior characterized by low biodegradability. Electrochemical techniques are recently gaining importance to address such problems due to their efficient and vigorous performance at ambient situations in the treatment of industrial wastewater (Radjenovic et al., 2015). For tannery wastewater

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therapy, mainly EO, EC, electro-Fenton (EF), and photoelectron-Fenton (PEF) procedures are the interest of electrochemical techniques. Various bench-scale studies are undertaken to reveal the efficiency of EO in treatment of the tannery wastewater effluent. The main attention is on the option of anode material and to regulate the optimal conditions of operable parameters (current density, temperature, pH, etc.) on the reaction mechanism of the electrochemical decay of unwanted pollutants (Vijayalakshmi et al., 2011). Total tannic acid and DOC eliminates under the same electrolytic conditions attain for equal energy consumptions. The following step is to find out the optimal conditions of the electrochemical parameters that give the highest pollutant eviction rate (Hammami et al., 2009).

- **Petrochemical, petroleum, and petroleum derivatives effluent:** Electrochemical approach of techniques applies in the application of upstream and downstream petroleum wastewater, regarding the large volume of water demands and its dangerous effects to the ecosystem. Usually, these wastewaters present a mixture of hydrocarbons and evaluate as total petroleum hydrocarbon (TPH) because the evaluation of each hydrocarbon separately is not practical. TPH evaluation is the result of the total sum of volatile petroleum hydrocarbons and elicits petroleum hydrocarbons (Iturbe et al., 2005). Due to the low concentration of BTEX in petroleum effluent, their expulsion by conventional wastewater treatments is tough and those last largely in the aquatic environment. In the upstream oil sector, for example, produced water (PW) is considered one of the most plentiful waste streams in the production of petroleum, oil, and gas, especially in the drilling and extraction operations (Abdelwahab et al., 2009). Anodic oxidation of real PW generates from the petroleum exploration of a petroleum plant in Tunisia using PbO_2 supports on tantalum and BDD anodes in an electrolytic batch cell (Gargouri et al., 2014). Three classes of PW (fresh, brine, and saline) generated by petrochemical industry are treated by EO with Ti/IrO_2-$Ta_2O_5$and BDD electrodes in a flow reactor (da Silva et al., 2013). Although in the presence of chloride, the two electrode materials show adequate results in the EO process where the pollutants removal is attained by both electrocatalytic materials and the identification and quantification of poisonous chlorine derivatives desirable before the actual application of EO. Large volumes of wastewaters too generate in the downstream of oil sector. The refinery processes, particularly distillation, hydrotreating, desalting, and cooling systems, use huge amount of water (Yavuz et al., 2010). The efficiency of Ti/RuO_2 anode in oxidizing organic substances present in wastewaters from petroleum industry before their discharge or rework (Santos et al., 2013).
- **Other industrial wastewater effluents:** The electrochemical treatment methods also apply to wastewaters that are generated by several industries such as food, pharmaceutical, power generation, and especially chemical industries. In almond industry, Ti/RuO_2 anode with Cl_2 electrogeneration is

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used for the EO of organic pollutants in wastewater effluents (Valero et al., 2014). As electrochemical oxidation is not appropriate to apply on effluents that contain high quantity of postponed solids such as that from the almond industry, the group preprocess the effluents by electrocoagulation (Zhu et al., 2009). Coking wastewater is produced from a scale of processes, namely, coal coking, coal gas distillation, and by-product recovery procedures of coking. Coking wastewater contains inorganic contaminants (ammonium, cyanide, sulfate, thiocyanate) and organic pollutants (phenolic compounds, polynuclear aromatic hydrocarbons or PAHs, nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds). Utilising BDD anodes achieves much higher DOC and NH_3–N removal rates than those of the latter electrochemical systems, with the potential to reduce treatment energy consumption by 40%, under experimental conditions of current density 20−60 mA/cm^2, pH at 3−11, at 20−60°C. Among the effluents, the bulk drug-constructing unit of the pharmaceutical industry appears much higher present efficiency on the removal of COD than the other effluents (Rajkumar et al., 2004).

10. Process economy

The main reagent of electrochemical technology is electron. Due to the presence of electron or "clean reagent," electrochemical technology can meet excessive environmental compatibility. High operating cost on energy consumption is the main challenge of this technology. There are only few researchers who reported a comprehensive economic analysis of the electrochemical operation (Kobya et al., 2009). The economic aspect of the electrochemical process of industrial effluents treatment is divided into direct and indirect costs including electricity, material, sludge transportation and disposal, labor, maintenance, and depreciation of equipment (Bayramoglu et al., 2007). The amount of energy consumed affects economic viability of the electrochemical process.

The cost can be calculated by Eq. 4.8.

$$Ec = (VIt/V_T) \tag{4.8}$$

In case of sacrificial anode, the consumed anode also can affect the cost. The cost can be calculated by Eq. 4.9.

$$m_e = (ItM/zFV_T) \tag{4.9}$$

Here, the electrical energy consumed per unit volume of treated effluent (kWh/m^3) is denoted by Ec. Electric current is denoted by I. V is cell voltage. Electrolysis time is denoted by t. Volume of the treated effluent (m^3) is denoted by Vr. me is the mass (g) of the sacrificial anode. Molecular weight (g/mol) of the electrode is M. Number of electrons involved is denoted by z. F is the

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Faraday constant. The sum of Ec and me by factoring these with the cost of electricity, and the cost per gram of the electrode is the total cost of process (Maarof et al., 2017). The cost of recovery Cr from electrocoagulation is 1.64 USD/m^3 (Espinoza-Quinones et al., 2009). To recover Fe, Al, Ca, Mg, Si, B, Pb, Cr, Mn, Zn, electrocoagulation 0.32−0.69 USD/m^3 is needed (Oncel et al., 2013). To reduce the electrical energy utilization for the electrolytic removal and recovery of metals, some efforts are taken. Alternative source of electrical power can reduce the operational cost (Maarof et al., 2017).

11. Conclusions

The growing environmental concern and the consciousness of the society of the health problems and ecosystem effects of industrial effluents and other water streams are incentivising water treatment technology enlargement. One of the great challenges nowadays is the systematic removal of organic contaminants from water bodies that can be hardly eliminated by conventional techniques. The electrochemical technologies and the electrochemical advanced oxidation procedures are potential and encouraging alternatives for wastewater treatment, which reveals high organic removal. Between them the electrochemical oxidation is one of the most promising procedures. The utmost outstanding outcomes are the complete removal of constant organic contaminants and the broad range of application of this technology. The mixture of this electrochemical procedure as prepost- or combined treatment opens a vast scope of novel and increased procedures. An electrocatalytic anodic material needs to try to decrease the initial investments on the addition of electrodes (Garcia-Segura et al., 2018). The advantages of the electrochemical methods include lower operating costs and less usage of extra chemical reagents and simultaneous achievements of fairly pure metals and elimination of organic pollutants. The primary benefit lies in the electrochemical method's easy control over treating metal wastewater and simultaneous removal of organic compounds. More economical and active electrodes for the treatment of special pollution, advanced process condition, and more effective current should be investigated (Chen et al., 2013). Due to judicious and effective nature of electrochemistry, there are appreciable advantages of electrochemical metal recovery contrasts to other conventional recovery methods, such as they are biodegradable without or restricted secondary pollution generation, need no extra chemical reductant/oxidant, readily combine with other materials or technologies, require only simple treatment with excessive clarity products, and also show variability in unlike electrolytes or temperatures. To attain electrochemical metal recovery rather than removal, further purification preparatory treatments, selective and stepwise extraction, ion-selective membrane are engaged to present better metalloid or metal items. Some specific advances and challenges of different electrochemical and metal recovery methods have been emphasized for further information.

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- Most important and empirical electrochemical metal recovery technique is known as electrodeposition, which mostly originates from long history and growth of electrometallurgy. Other types of electrowinning, electrorefining, and muddy electrolysis employ in different climates, reactors, and electrolytes for several metal ions and impure metal alloy/sulfide/oxide recovery from complex wastes.
- Electrosorption attracts increasing attention due to its easily charge and discharge properties, porous nanomaterial electrode development, and previous desalination experiences. The introduction of membranes alleviate the "common-ion effects" and facilitate the desorption/adsorption, while the integration of Faradic/capacitive electrodes and flow systems provides further enhancement. Charge and discharge feasibility and durability require further guarantees. Most recent electrosorption research concentrates on the heavy metal pollution remediation of this technique.
- EDI and electrodialysis are electricity-driven membrane separation processes; the target metal ions selectively concentrate/recover and purify water without secondary pollution generation. The synergistic effect between electricity and membrane is highly important for this technology, particularly for the separation efficiency considerations and separation rate (Jin et al., 2020).
- EC is an appealing process for the treatment of several types of wastewater, by virtue of numerous benefits including environmental adaptability, energy effectivity, ability, security, selectivity, and cost efficacious. This procedure is identified by simple equipment, easy action, less operating time, and reduced amount of sludge, which remains quickly and keeps less water. Further studies require executing to study the effect of shape and geometry of the electrodes to conceivably enhance the contaminant eliminates efficiency (Bazrafshan et al., 2015).

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Chapter 5

Scaling-up of bioelectrochemical process for simultaneous wastewater treatment and energy extraction

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Abstract

The use of microbial fuel cell (MFC) could take the place of traditional aerated activated sludge process. Because of this, each pilot study, field trial, or prototype installation adds to the body of knowledge that qualifies a technology for widespread use and practical deployment. The standard designs used in laboratories for their applications include the double-chamber, single-chamber, up-flow, and stacked MFC. For various applications, including bioelectricity generation, wastewater treatment, bioremediation of hazardous substances, biohydrogen production, and biosensors, the type of electrode materials and proton exchange membrane employed in MFCs play a crucial role in the performance. This chapter makes it easier for the reader to comprehend significant developments in the scaling up of MFCs. Before contemplating this technology for widespread field applications, several analytical methods, structurally and morphologically modified electrode materials, hydraulic and electrical stacking of multiple units, power optimization techniques and significant improvements in the developed novel materials, have been carefully discussed to show the key challenges that must be resolved to make the MFC technology practicable.

Keywords

Bioelectricity generation; Microbial fuel cells; Proton exchange membrane; Wastewater treatment.

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1. Overview of the technology

Although Michael Potter first introduced the microbial fuel Cell (MFC) technique in 1911, awareness of and interest in this kind of environmentally conscious technique continues to grow. Bioelectrochemical systems (BESs) were born from microbial-derived electrochemistry and take advantage of the bioelectrochemical usage of organic materials through microbial metabolism to produce usable bioelectricity and fuels. BES has a variety of classifications, including MFC, microbial desalination cell (MDC), and microbial electrolysis cells (MECs), although only the MFC is specifically engineered to produce direct current from the breakdown of various substrates and waste sources. The MFC is a promising substitute to the conventionally used aerated activated wastewater treatment technique as it generates power along with simultaneously treating the feedstock. As such, every pilot study, field experiment, or prototype installation adds to the corpus of information that makes a technology ready for wider market adoption and real-world application. A significant amount of literature (Choudhury et al., 2017) focuses on lab-assisted systems, analytical techniques, and performance enhancements made possible by novel materials. However, because of the complexity of the installation and operation process along with other engineering and environmental dependable variables, pilot studies are unusual. The first MFC stack was created by Barnett Cohen in 1931 when he connected several 10 mL bacteria-based fuel cells together in series to produce a total of 2 mA and 35 V. Since then, the performance of the MFC has been amply improved but rarely put into use in actual contexts.

The reactor architecture and each of its constituent parts have an impact on performance of MFC (Bhowmick et al., 2019; Das, Das, Sharma et al., 2020; Jadhav et al., 2020; Jadhav & Ghangrekar, 2009; Sharma, Das, Chakraborty et al., 2023). As MFCs can be utilized in a pilot application for power generation, and sensing, all of these depend on the requirements of the individual applications, and this research is basically concerned with system efficacy and price. The development of anode material suitable for MFCs must meet the requirements of high electrical conductivity, improved surface area, and biocompatibility that would enable effective electrochemical 'wiring' of living bacterial cells, as well as high conductivity, corrosion resistance, and chemical stability with low cost as the main driving factor. Anode is a crucial component in terms of the surface area available for the growth of the microbial biofilm, and to satisfy all the requirements, carbon-based materials typically come in the form of granular or fabric-based materials such as cloth, mesh, or felt. According to research, improving the anode packing and the anodic surface area-to-volume ratio will enable a cost-effective increase in power density of MFC. In addition to improving power production, such modifications can improve the effectiveness of degradation of the pollutants and the treatment efficiency of the process. A promising alternative to anode is the

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creation of new inexpensive solutions, such as carbon sponge or stainless steel wool, which has to be tested in lengthy studies.

The reduction reaction that takes place in the cathodic half-cell is the foundation for optimizing cathode components. An important source of losses is the oxygen−reduction reaction (ORR) occurring at the cathode of MFC, which is frequently the limiting reaction. An air-breathing cathode is the most practical cathode configuration for large-scale MFC applications; however, it performs poorly in static operation mode. This is frequently related to the gradual deactivation of the cathode scaling with deposited salts. To prevent salt precipitation, the cathodic chamber must then be configured appropriately (Sharma et al., 2021, 2022). This chapter facilitates the reader to understand the major advancements in scaling-up of the MFCs. Various parameters including membranes, electrode materials, operating conditions, and catalysts have been thoroughly discussed to illustrate properly the major issues, which needs to be addressed before considering this technology for large-scale field applications. This chapter would surely help the reader to understand the fundamentals of the technology, and present a clear view on the major challenges and possible solutions to make the MFC technology viable.

2. Types of MFC

The MFC is among the most attractive technologies explored by researchers for simultaneous sustainable energy extraction and treatment of wastewater generated from various sources. As discussed in the previous sections, the technology utilizes the chemical energy of the organic matter to generate electric energy. Generally, the MFC consists of a conducting anode and cathode, and a membrane. A suitable catalyst is employed as the cathode to increase the rate of ORR when oxygen is used as an electron acceptor. The anodic modifications on the other hand facilitate the formation of the biofilm, reduce the start-up time of the MFC, promote the electron transfer mechanism, and also reduce the internal resistance of the cell (Mittal & Kumar, 2022; Singh & Kalia, 2017). On the basis of the configurations, the MFCs are classified as discussed in the following.

2.1 Double-chamber MFC

A double-chambered MFC consists of two chambers, anode and cathode, separated by a high-performance proton exchange membrane (PEM) (Fig. 5.1). It is considered as the simplest design among the several designs of the MFCs (Niessen et al., 2004). Generally, for a double-chambered MFC, a defined medium in the anodic compartment and a defined catholyte mixture are employed for simultaneously treating wastewater as well as generating

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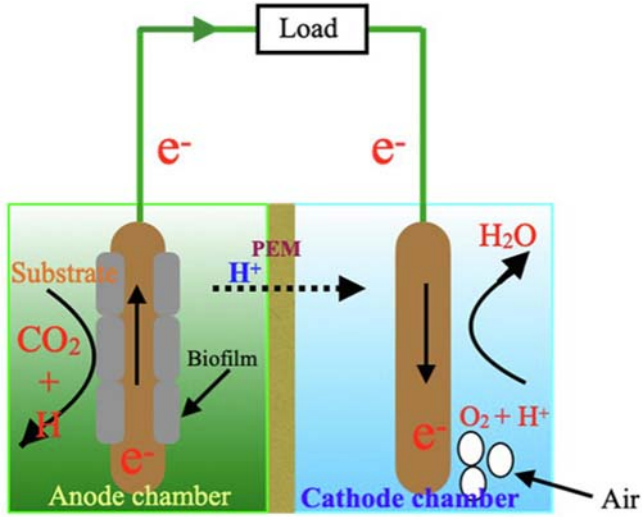

FIGURE 5.1 Schematic represntation of double-chambered MFC.

clean energy. Usually the air cathode MFC consists of exposed cathode to facilitate the electron acceptance property. This type of MFCs may serve as a valuable source for generating clean energy in remote sensing regions.

2.2 Single-chamber MFC

As depicted in Fig. 5.2, single-chamber MFC essentially consists of only one chamber, which consists of both anode and the cathode. In this MFC, the anode is placed at a distance or closer to the cathode separated using a specialized membrane, called as PEM. Studies suggest that reducing the distance between the electrodes, the internal ohmic resistance can also be reduced. This can be obtained with the help of employing the catholyte by connecting the two chambers, thereby enhancing the power density. This type of MFC is comparatively simple in structure, it is much more economical as compared with the double-chambered MFC, and produces much more power than the double-chambered MFC (Das et al., 2018; Jadhav et al., 2020).

2.3 Up-flow MFC

This design of MFC was initially developed by Jang et al. (2004). It basically consists of a cylindrical structure, which employees cathode at the top, whereas anode resides at the lower part of the structure. The chambers are apportioned using glass wool and the bed layers made up of the glass. The substrate is given from the bottom most part (i.e., anode) and rises up to the cathode, as illustrated in Fig. 5.3. The gradient is developed among the two electrodes, facilitating

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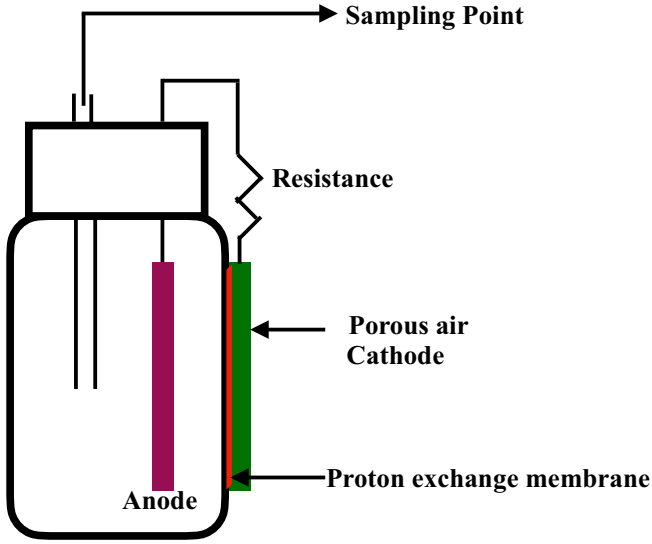

FIGURE 5.2 A single-chambered MFC.

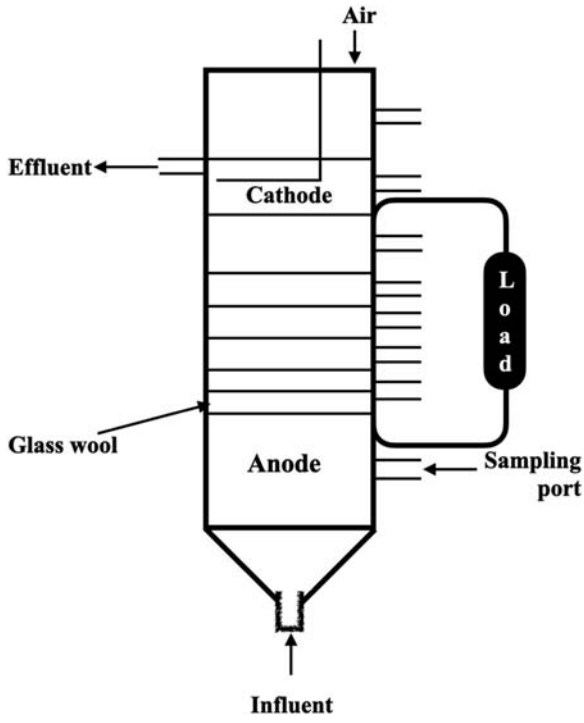

FIGURE 5.3 A schematic diagram of an up-flow MFC.

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the favorable action of the MFC. This type of MFC has no partition, and hence, complications related to proton transmission are rare (Zhou et al., 2013). These types of MFC are suitable for wastewater treatment process due to ease of up-scaling when compared with the other designs of MFCs. However, the main obstacle exists in the energy involved in pumping the substrate (Zhou et al., 2013). This infers that the fundamental objective of this type of MFC is to treat the wastewater, and not to generate sustainable energy.

2.4 Stacked MFC

As illustrated in Fig. 5.4, a combination of several number of MFCs, which are connected together either in series or parallel combinations to enhance the output power, is called as stacked MFC (Logan et al., 2006). The MFCs output enhances when individual power output of the cells or the current output is multiplied. Essentially a single unit of MFC can generate maximum 0.8 V of open-circuit voltage (OCV) (Logan, 2005). Hence, combining the individual cells in either series or parallel combinations may lead to achieving higher resultant power. However, several other factors play a crucial role in generating current in a stacked MFC (Zhou et al., 2013). Voltage reversal (VR) is mainly regarded as the main reason for limiting the performance of the stacked

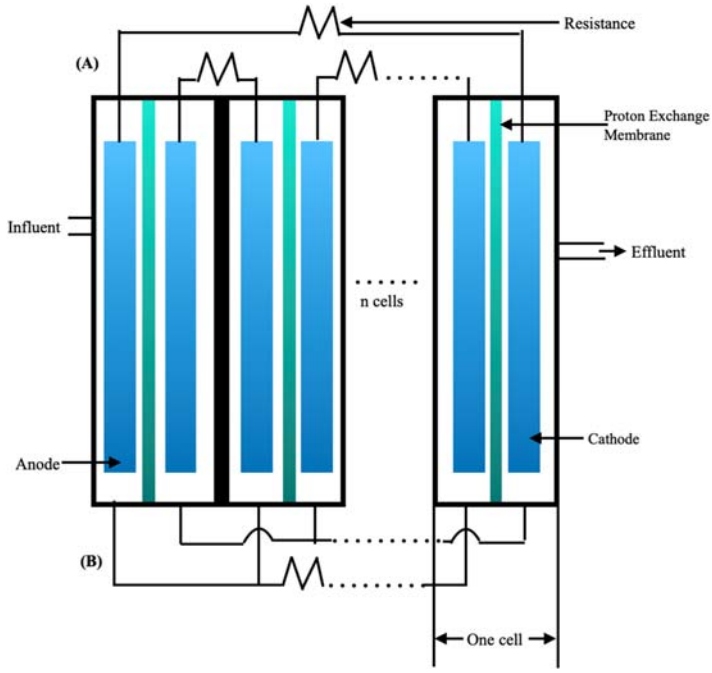

FIGURE 5.4 A schematic diagram of a stack MFC.

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MFCs. During VR, the voltage of a unit cell is reversed in a system operated in series connection, and this drops the voltage and reduces the total output of the complete system. The MFCs connected parallelly tends to generate more power when compared with the series-connected MFCs. Therefore, it can be interpreted that, for parallelly connected stacked MFCs, higher bio-electrochemical reaction rate is attained in comparison with the stacked MFCs connected in series.

The MFC's coulombic efficiency (CE) illustrates its ability to transfer electrons from the anode side to the cathode and hence generate electric current. Studies suggests that the stacked MFCs achieved much better CE values when operated in parallel mode. The major challenge to address in the stacking of MFCs is the voltage reversal, which may occur due to the substrate depletion in the cell, which leads to the diminished ability of the bacteria to generate greater voltage (Logan et al., 2006).

3. Factors affecting the performance of MFC

As discussed in the previous sections, there are various factors that affect the performance of the MFCs. These factors include the materials used for the electrodes preparations, the catalysts involved, the employed PEM, and the operational conditions. The operational conditions include the effect of pH, temperature, feed rate, and the shear stress.

3.1 Materials for the electrodes

The anode and the cathode play a crucial role in effective treatment and generation of electric current from the MFCs. The materials selected for the preparation of the anode and cathode should be conductive in nature, must possess antifouling property to the bacteria (for anode), and most importantly, it must be cheaper (Eisa, 2023). Further, the electrode materials must possess higher surface area to enhance the performance of the MFCs (Zhang et al., 2012). Researchers have extensively explored the possibility of designing better electrodes for enhancing the performance of the MFCs. The modifications include addition of several nanomaterials, which have successfully increased the power generation capacity several folds. The focus in doping catalysts on the anode is to promote the formation of the biofilm, thereby enhancing the electron transfer process (Bhowmick et al., 2019; Das, Das, Sharma, et al., 2020). Several investigations demonstrated the implementation of the nanomaterials for increasing the electrical conductivity at the interface of the biofilm and the electrodes. For instance, platinum (Pt) has shown to deliver better electric current values when compared with the bare cathodes (Bond & Lovley, 2003), and has been considered as the best catalyst for reduction of the oxygen in the MFCs; however, its high cost remains a major hindrance for its applications.

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3.2 Proton exchange membrane

A PEM is a selective barrier, which allows preferential transport of species, along with maintaining an effective separation between the anode and the cathode (Samanta et al., 2023; Sharma, Samanta et al., 2023; Sharma, Pramanik et al., 2023; Sharma, Das, & Purkait, 2023; Sharma et al., 2022). As illustrated in Table 5.1, a good PEM exhibits high proton conductivity, possesses effective stability in harsh chemical environments, should be mechanically strong, and must be cost-effective to be useful for the field-scale applications (Bu, 2023). It has pores inheriting charged side walls that promote the transportation of the protons from anodic compartment to the cathodic compartment. During the MFC's operation, a diffusion of the anolyte across the separator to the catholyte may lead to its fouling. This can potentially block the passage of the protons to the cathode and thereby decrease the output power of the MFCs. Further, the movement of the catholyte to the anodic compartment may hamper the involved bacteria's performance. For instance, considering oxygen as the electron acceptor, its diffusion to the anodic chamber could potentially hamper the growth of the biofilm of the anaerobic bacteria. This can affect the overall performance of the MFCs (Reguera et al., 2005).

TABLE 5.1 Several proton exchange membranes used for MFC study.

Membrane	Cathode	Power density (mW/m^2)	References
Textile separator was made from 46% cellulose and 54% polyester	Carbon cloth coated with Pt/C	120	Ahn et al. (2013)
Nafion 117	Pt/C	47.6	Venkatesan and Dharmalingam (2015)
Sulfonated polyphenylene sulfide	Carbon cloth coated with Pt/C	190	Moon et al. (2015)
5% goethite-blended clay ware membrane	Carbon felt	112.8	Das, Das, Dixit, et al. (2020)
PTDPBSH-70	Carbon felt coated with Pt/C	226	Ghorai et al. (2021)
PTPFBSH-90	Carbon felt coated with Pt/C	312.50	Ghorai et al. (2020)
WCA-3	Carbon cloth	150.22	Sharma et al. (2021)

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The PEM also increases the MFC's internal resistance and leads to the diffusion of the ions or the electrolytes, leading to the concentration polarization loss of the process. Nafion membrane has been widely used PEM in the MFC due to its permeable selectivity toward the protons. In a study conducted by Sharma et al. (2021, 2022), various PEMs were prepared where nanoparticles such as graphene oxide (GO) and reduced graphene oxide were used to enhance the performance of the MFCs for simultaneous treatment of municipal wastewater and sustainable energy generation (Sharma, Das et al., 2023; Sharma, Mondal et al., 2023; Singh et al., 2023). PEMs successfully maintain the neutrality of the charges between the anolyte and the catholyte (Raghavulu et al., 2013). Further, the percentage exposure of the membrane surface area also plays a critical role in achieving high power output from the MFCs. However, it is very essential to address the cost issues of the PEMs, as high cost of the membranes is a major hindrance for large-scale application of the process (Jadhav, Park, Eisa et al., 2022).

3.3 Operating conditions

Several parameters such as pH, temperature, feed rate, and shear stress also play a critical role in determining achievable power from the MFCs. As discussed in the previous sections, the microorganisms oxidize the organic substrates and generate protons, which are transported to the cathode with the help of PEM, where they mix with the electrons and the electron acceptor to promote the formation of the water. Post a long course of operation of the MFC, the concentration of the protons gets raised significantly in the anolyte. Because of the limited proton movement across the PEM, the accumulation of the protons turns the anodic chamber more acidic and makes it inappropriate for the further growth of the bacteria. Since the active bacteria are more active at the neutral pH, the performance of the MFC decreases (Venkata Mohan et al., 2008).

On the other side the alkalinity of the catholyte increases because of the unavailability of the protons replacement via the oxidation process and constant diminution of the protons by the reduction reaction (He et al., 2006). The high pH value of the catholyte leads to the reduction in the generated current. Further, the ability to reduce oxygen increases with a declination in the value of the pH. Hence, low pH value is considered appropriate for the reduction of oxygen to achieve better current values from the MFCs (Niessen et al., 2004). Maintaining pH value of electrolyte in the anodic compartment is one of the most crucial conditions for proper growth of the bacteria, affecting the metabolic activities of the microbes, and thereby alters the mechanism of the generation of protons and the electrons. An investigation conducted by the Bermek et al. (2014) suggests that MFCs operated at lower anodic pH values demonstrated enhanced proton transfer rates; therefore, more protons transfered at the cathode side, which reduced the current density

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further. However, it was also later revealed that, the pH ranging from 6 to 9 is suitable for the growth of the microbes and achieving higher power outputs.

Further, it becomes more suitable to sustain two variable pH conditions in a double-chambered MFC for optimizing the anodic and the cathodic reactions (Huang et al., 2012). It further becomes more difficult in maintaining the pH in the MFC with air cathode due to the availability of the single electrolyte present in the anodic compartment. It was observed that air cathode MFC can be successfully operated maintaining the pH of the anolyte in the range of 8−10 (Bermek et al., 2014). The results illustrates that the anodic bacterial activity was optimum at a neutral pH, whereas the oxygen reduction reaction was amended at higher pH value.

The other parameter effecting the operation of the MFCs is the operating temperature. The operating temperature affects the kinetics of the complete system. A greater deviation in the temperature at the time of operating the MFC may lead to variation in the performance of the MFC to a great extent. The operating temperature affects the metabolism of the microorganism, mass transfer rate, and the related thermodynamics. It is considered as a crucial parameter for the wastewater treatment and sustainable energy generation using MFC (Amend & Shock, 2001). Generally, the MFCs are operated at the ambient temperature ranging from 25 to 30°C. However, studies also demonstrate that higher power density and COD removal efficiencies can be achieved at greater temperature values (Jafary et al., 2013). This may be attributed to the augmentation of the bacterial metabolism and the permeability of the employed membrane. The higher temperature can enhance the anolyte and the catholyte conductivity, thereby decreasing the MFC's ohmic resistance, leading to elevated power density values. In a similar study conducted by Yang et al. (2015), it was illustrated that the temperature range between 30 and 45°C is more appropriate for achieving better power outputs. This is attributed to the fact that the bacterial biofilm demonstrated peak catalytic activity at the mentioned temperature range. However, postformation of a stable biofilm, the available microorganism can adjust their metabolism within a small variation range in the temperature.

Feed rate and shear stress are other parameters that can affect the output performance of the MFCs. Two different modes of operations are viable for the MFCs, which include batch mode of operation and continuous mode of operation. The batch mode of operation relates to the one where substrate is given during the initiation of the cycle, whereas for the continuous mode of operation, the substrate is continuously provided at short time intervals. The MFC operating in the continuous mode exhibits the hydrodynamic problems, which affects the overall performance of the MFC. Hence, the flow rate and the related hydraulic retention time (HRT) along with the shear stress are essential parameters, which needs to be optimized for obtaining better performance from the MFCs (Venkata Mohan et al., 2014). Investigations advocate that higher flow rates causes declination in the obtained output

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power along with the COD removal and the coulombic efficiency (Sun et al., 2014). Investigations also demonstrate that considerably lower value of shear stress promotes the formation of the denser biofilms, which further corresponds to the formation of the stable attachment of the bacteria on the anode. The MFCs operation at variable shear stress may lead to the growth of different types of bacteria at the anode side. However, studies also suggest that greater shear rates in the MFCs reduce the diversity of the formed microorganisms, promoting in the formation of the homogenous biofilms (Ringeisen et al., 2006).

4. Scaling-up of MFC

4.1 Miniaturized MFC

With an increase in the physical size of the reactor, power and current density substantially decreases (Ieropoulos et al., 2010). For example, a module made up of two MFC units and having a total volume of 250 L attained a rather reduced power density of 0.47 W/m^3. This is a result of the anode, cathode, membrane, and electrolyte components' increased internal resistance. Increased power densities are made possible by the miniaturization of MFCs, which can be used in MFC stack. The reactor should be composed of modules with multiple electrodes and/or several MFC units to get around the practical difficulties. Stepping up the voltage values when coupled in series to prevent short circuiting requires division into modules (components of the entire system), hydraulic isolation of such modules, and multiplication of units. Here, the modularity is represented by the components of the module's (i.e., anode and cathode), which can be electrically connected in parallel because they share the same electrolyte, thereby forming a collection of multiple MFC units.

4.2 Large-scale MFC

The generated output power from an individual MFC unit is not enough for majority of the practical applications (Jadhav, Park, Pandit, et al., 2022). In practice, the efforts to develop stacked MFCs connected in series have yielded performances below expectations. Large-scale prototypes can be tested using a variety of techniques. Pilot experiments recently showed the combination of a membrane-less 40-L stack into a municipal wastewater treatment facility, which demonstrated stability even when operating at low chemical oxygen demand (COD) concentrations. A 70 L stack of five membrane-based MFC unit was also investigated, where a power density of 51.5 W/m^3 was achieved; however, electrical current losses were experienced in the parallel circuit combinations. A cloth separator was utilized in a pilot research that employed brewery effluent with a total volume of 90 L, to restrict short-circuiting among

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the anode and the cathode, and the generated electricity was used to power the pumping mechanism. Ge and He reported that for implementing 200 L volume of stack to treat primary effluent, 77% of total COD was removed using electricity produced to drive the catholyte recirculation pump (Ge & He, 2016).

5. Stacking as a means for upscaling

MFC is still in the analysis and assessment stage at the laboratory level; however, some innovative new designs have been created recently to combine MFCs into practical applications. To increase the number of MFC components, this also involves the development of stackable unit. By connecting numerous units/modules that share a common fuel input route in a low through system, MFCs can be stacked for wastewater treatment purposes. The tubular technique is an option, and by connecting 5 units in a parallel connection, it was possible to remove up to 77% of COD and get up to 175.7 W/m^2 (Zhuang, Yuan, et al., 2012). The systems experienced an OCV loss when connected, both electrically and hydraulically, when the two similar MFCs were joined in series. The construction of 40 MFCs in a serpentine-like pattern improved the voltage to 23 V; however, the performance degraded with time (Zhuang, Zheng, et al., 2012) due to salt deposits deactivating the cathode. The first MFC pilot was carried out at Foster's brewery in Yatala, Queensland, in 2008. It encountered significant difficulties due to the accumulation of salts and biofilm (Liang et al., 2018), which is a frequent issue in long-term operation, particularly when an outside, open to air cathode is used. Employing an inverted design where the cathode is on the inside of the tubular reactor, insulating it from evaporation, or using a partially submerged cathode to keep it suitably hydrated are two ways to get around this (Walter et al., 2018). The stability of current generation and internal resistance, which are the main difficulties pertinent to the pilot studies, are two practical considerations for long-term operation. The kind of effluent being processed, with its particular organic loading, pH, chemical composition, and salinity, as well as the electrode material, all of which have an impact on the system's internal resistance, influence the bacterial community. Therefore, the prototype should be created in accordance with the specific task, environment, and substrate processing type and low rate that it will be used for.

6. Manufacturing and cost analysis

All of the aforementioned information has been provided under controlled circumstances from a fundamental science lab-based perspective. The biggest obstacle to a technology's adoption in the actual world is whether it can be manufactured, which leads to economies of scale. The same is true for MFC development, and this has contributed to the difficulty in the

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technology's adoption and economic viability. Even at the prototype stage, the majority of the basic elements and components can be customized and hence expensive. It is a scientific problem to find alternatives that would (1) operate just as well and for longer periods of time, but most crucially (2) be economical and broadly accessible. Alternate low-cost material such as ceramic or card stock and plant-derived electrodes (Liang et al., 2018) are areas where researchers have looked into. Ge and He stated that almost 55% of the material cost of the MFCs was attributable to the cation exchange membrane in their long-term operation of their pilot research in wastewater treatment plant (Ge & He, 2016); therefore, less expensive separators such as ceramics are a viable alternate for this technique. The accessibility of the system components (electrodes, membranes, and wiring among others) is a crucial element if the technology is to be assembled and applied on a larger scale, say 1000 units or more. The MFC field would gain from this in terms of in situ expertise and real-time data collection. Pollutant degradation and electricity production are both possible using MFC reactors, simultaneously. In a study conducted by Walter et al. in 2018, a novel designed MFC employing undiluted urine was investigated. Investigation suggests that with 44 h retention time, a four-module cascade continuously produced power of around 150 mW (Walter et al., 2018). This does not account for the savings that would be realized for each liter of wastewater treated and is based on raw power statistics generated throughout the field trial in which the MFC stack was run on neat human urine.

7. Environmental aspects, challenges, and future perspective

The techniques from sustainable energy generation and wastewater treatment have not demonstrated any crucial potential threat to the environment. As the technology involved the conversion of chemical energy of the organic matter to the electric energy, this technology is a clean source of energy. A wide range of studies involving basic science for the prototypes prepared with the lab-scale perspective have been conducive with the initial technological developments. The investigations were conducted in the controlled environment, which do not exactly replicate the actual conditions required for operating the process at the large scale. The bigger technological challenge is to achieve the manufacturing suitability of the process for driving the scale economies. This has been until now a major challenge in the development of the MFC to be available for large-scale applications. The majority of the core components of the MFC can be spoken and are costlier even at bench-scale prototype level. Henceforth, it is essential to address the major challenges to achieve the process to perform continuously for a longer duration of time. It also becomes equally important to achieve a technological advancement, which could be cost-effective and viable. The major technological achievements made include

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the development of the ceramic PEMs, which are better substitutes for costly membranes (Jadhav et al., 2017). Other advancements include the designing of the plant-based electrodes (Chen, Chen, et al., 2012). In an investigation conducted by Ge and He for the long durational operation of their pilot study for treating wastewater, over 60% of the total material cost included the cost for the PEM (Chen, He, et al., 2012); hence, cost-effective ceramic separators are suitable alternatives to reduce the overall operational cost of the process. Several other crucial factors effecting the economic viability of the process include the availability of the components of the system such as electrodes, wiring, etc. for assembling and implementing the process in the larger scale (Jadhav, Chendake et al., 2022). Further, it becomes very important to take note of the issues and the information from the small bench-scale experiments for assessing the technological viability of the MFC process in a realistic environment such as temperature/organic loading/humidity/pH and under several operating variables including retention time, flow rate, continuous or batch flow. This would indeed be beneficial for the real-time data collection of the MFC data and in situ knowledge. The biggest advantage of the MFC reactors is that it can degrade the pollutants and can simultaneously produce electricity, and thereby potentially reduce the cost, consumption of the energy, and the treatment cycle.

Preparation of the high performance and cost-effective membranes is also a crucial process to make the technology viable. In a similar investigation conducted by Sharma et al., ameliorated PEMs were prepared using cellulose acetate obtained from agro waste and GO prepared using Taylors method. The membranes demonstrated excellent properties and were cost-effective for bench-scale operations. However, further progress is required to employ similar membranes for large-scale operations, to develop the novel energy harvesting technology. Further, in the energy storage process, the implementation of the external capacitors has been done in several investigations. Studies suggest that implementation of the internal supercapacitors may prove to be a novel way to enhance the output power (Bhowmick et al., 2019; Chakraborty et al., 2020; Jadhav et al., 2014). The innovation is moving toward broader acceptance and the market thanks to the knowledge acquired on the current pilot studies and implementation attempts (Santoro et al., 2018).

8. Conclusion

Only the MFC is capable of breaking down the waste and simultaneously generate electricity. Newer advancements must focus on applicability of the technology and designing the process in such a way that it can successfully achieve the criteria for performing better, and most importantly, it must be viable in the realistic conditions. The basic technological advancement of the future MFC is toward increasing the size of the units along with the ability to

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multiply the units with the help of modularity to overcome the limitations of the transport and ohmic loses instead of increasing the size of the single unit. Secondly, it is the design of the scaled-up units through compacting the system footprint to attain greater power densities, but at the same time making it functional and applicable for practical applications. Thirdly, for ensuring the systems longevity along with its components, ensuring them resistant to fouling, corrosion, and upscaling. Finally, recent developments must focus on including power management systems for MFCs, and focus should be made on employing energy generation and storage systems such as supercapacitors for increasing the overall performance of the system for real-life large-scale applications.

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Chapter 6

Recent advancement and application of environmental electrochemistry

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Abstract
Water scarcity, groundwater depletion, and surface water pollution have become some of the major challenges for environmental engineers in the 21st century. Thus, wastewater treatment becomes crucial to maintaining the quality of surface water sources. Large cities and industries are the major contributors to wastewater, and this large amount of wastewater must be treated partially or completely before discharging into any water body. As land availability is a practical issue, compact wastewater treatment plant is the need of the hour. Electrochemical treatment can be put to work in such cases. Electrocoagulation, electrodialysis, and electrooxidation can be used to treat wastewater at a faster rate than conventional treatment processes. Thus, it requires a lesser plant footprint for treating the same volume of wastewater. Besides, water scarcity energy shortage is inevitable because of rapid urbanization and industrialization. Therefore, researchers should focus on harvesting the untapped energy present in wastewater in form of chemical energy. The bioelectrochemical system serves this purpose by oxidizing the organic waste present in the wastewater by employing microbes as a catalyst. Microbial fuel cell, microbial electrolysis cell, microbial electrosynthesis, enzymatic fuel cell, microbial solar cell, plant microbial fuel cell, and microbial desalination cell are different types of bioelectrochemical systems that are employed for not only treating wastewater but also generating electricity, producing value-added by-product and desalination of water. This chapter focuses on recent advancements and applications of electrochemical technology and bioelectrochemical system.

Keywords
Bioelectrochemical systems; Electrochemical technology; Electrochemistry; Electrocoagulation; Microbial fuel cell.

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1. Introduction

Since the 20th century, significant environmental pollution induced by industrialization has had a negative influence on the atmosphere, water, and soils. As a result, treating water, wastewater, and soil have become a significant social, economic, and political issue. Organic, inorganic, and bacterial contaminants in municipal and industrial wastewater must be treated before being released into the environment. Pesticides, dyes, phenolic compounds, halogenated compounds, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), endocrine-disrupting chemicals (EDCs), and other refractory contaminants released into wastewaters require different strategies from the industry to treat. With a fast-expanding global population and growing environmental concerns, protecting the environment has emerged as a significant challenge and a key element for future technological advancement, which must adhere to the principles of sustainable development. Strategies for preserving the environment usually include ways to deal with waste and the innovation of new production technology or products that cause minimum damage to the environment or no damage at all. In addition to these issues, the globe needs to produce energy from sustainable sources. Electrochemistry plays a crucial role in both types of approaches. Electrochemical techniques can be used to recover or treat domestic and industrial wastewater. The development of bioelectrochemical systems (BESs) primarily aims to generate power as well as value-added chemicals. However, this literature tries to explore electrochemical procedures and equipment that can help create a better environment. Electrochemical processes for the treatment of wastewater containing organic and inorganic contaminants, recovery of nutrients and heavy metals, electricity production, and value-added chemical synthesis are discussed. Finally, the significance of electrochemical sensors in the monitoring of biological oxygen demand, water quality, and toxic chemicals is highlighted.

2. Electrochemistry

Chemical treatment of wastewater is an old technique to separate particles up to the desired level. The main drawback of such processes is the high cost of the chemicals required. The electric field–assisted or electrically powered chemical treatments reduce the cost and also the time for the process. Moreover, these processes can also be used in continuous mode. The wastewater from various industries containing color, heavy metals, and toxic elements can be treated by electrochemical processes. These processes may or may not require any type of membrane. For instance, the electrocoagulation process does not require any separation, while electrodialysis requires more than one membrane to separate different types and sizes of ion particles. Various electrochemical treatments, their mechanism, and applications are given in the following section.

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3. Electrochemical technology

3.1 Electrocoagulation

Coagulation is a process of colloidal particle removal by aggregating the small particle so that they can be settled down in the settling basin. The colloidal particles are mostly negatively charged so chemicals (e.g., alum or ferric chloride) are added to increase the concentration of positive ions that neutralize the colloidal particles and form larger settleable particles. But, the salinity of the water increases because of the coagulants added.

Electrocoagulation (EC) is the process of donation of positive ions (metal ions) by sacrificial anode and production of OH^- and H_2 from the cathode section. The process was proposed by Vik et al. (1984) (Nasrullah et al., 2019) who reported a treatment plant (in London built in 1889) that treated sewage by mixing it with seawater and electrolyzing it. J.T. Harries used sacrificial aluminum and iron anodes for wastewater treatment and got patent for it in 1909. Matteson et al. (1995) reported the process as "electric coagulation" in which electrochemically dissolved aluminum anode forms aluminum hydroxide by reacting with the hydroxide produced in the cathode. EC technology can be run using either AC or DC power supply (Nasrullah et al., 2019). However, the majority of the experiments use a DC power supply as power source. Many experimental works have been carried out on this process and concluded that EC is one of the effective processes to treat different industrial wastewater, agricultural wastewater, urban wastewater, arsenic-containing wastewater, and oil shale wastewater (Smoczyński et al., 2012).

The process mechanism mainly deals with the electric disintegration of Fe and Al anode acting as a coagulant (Smoczyński et al., 2012). These materials are used as there are abundant resources in the ground, and these are nontoxic and have a higher potential to remove pollutants. Commonly, both the anode and cathode are of the same material, but dissolution takes place only at the anode. The more the coagulant is added to the wastewater, the more electric double-layer distance decreases and the particles get attracted and aggregate to form settleable large flocs. The overall process has the following steps:

- Ion dissolution from metal anode
- Hydroxyl ions and hydrogen gas formation from cathode
- Reaction at the surface of the electrode
- Colloidal particles form larger particles influenced by the coagulant
- Flocs are removed by floatation or sedimentation

The effect of orientation of the electrodes were studied (Fig. 6.1) by many, and it is mostly reported that the vertical orientation as the most preferable for the electrocoagulation process (Majlesi et al., 2016). The oxidation of the metal occurs very quick between pH of 7 and 9.

$$2H_2O + 2e^- \rightarrow H_2\,(g) + 2HO^-\,(aq)$$

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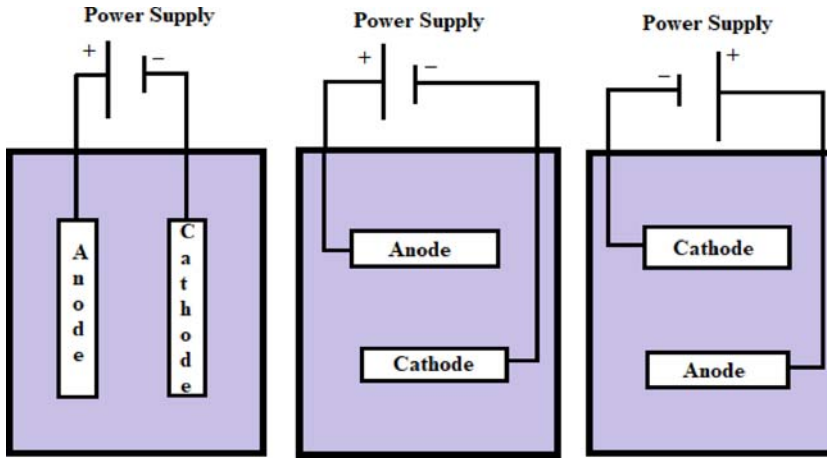

FIGURE 6.1 Different orientation of the electrodes.

$$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$$

The aluminum ions also dissolve from the cathode at higher pH as aluminate (Table 6.1).

$$2Al(s) + 6H_2O + 2HO^- \rightarrow 2\,[Al(OH)_4]^- (aq) + 3H_2 (g)$$

Some of the advantages of this process are as follows: higher organic load and high volume of wastewater can be treated, high efficiency from ion and colloidal matter removal, removal by electroflotation of particle with hydrogen bubbles, use of low-cost electrode. On the other hand, replacement of the electrode and production of sludge are some major drawbacks of this process.

TABLE 6.1 Reactions in anode and cathode.

Iron as electrode	Aluminum as electrode
Reaction in anode: $Fe \rightarrow Fe^{2+} + 2e^-$ $Fe \rightarrow Fe^{3+} + 3e^-$ Reaction in cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $3H_2O + 3e^- \rightarrow 1.5H_2 + 3OH^-$ So, during electrolysis, overall reaction take plays as follows: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)^2$ $Fe^{3+} + 3OH^- \rightarrow Fe(OH)^3$	Anode makes oxidation reaction: $Al \rightarrow Al^{3+} + 3e^-$ Cathode makes reduction reaction: $3H_2O + 3e^- \rightarrow 1.5H^2 + 3OH^-$ So, during electrolysis, overall reaction take plays as follows: $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

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3.2 Electrodialysis

The growing population is concerning with regard to the food supply and putting stress consequently on the fertilizer industry. Moreover, the limited potable water is also concerning. Recovery of nutrients and water from the wastewater can reduce the stress for now. But, most of the conventional treatment processes are not highly effective for this purpose. Electrodialysis (ED) is an electrochemical process that separates the ions using ion exchange membrane. It separates the ionic species and also organics from the electrolytes within an electric field. An ED consists of one anode and one cathode located at both extreme sides of the unit, and in between, several anion exchange membrane (AEM) and cation exchange membrane (CEM) are present. The electrically charged particles start to migrate in influence of the electric field. The anions of the influent move toward the anode and the cations toward the cathode. Cations can pass through the CEM, but they are blocked by the AEM, and on the other hand, anions can pass through the AEM but they are blocked by the CEM. This phenomenon increases the concentration of salt in concentrate compartment. The CEM covalently binds with the negatively charged groups such as carboxylic acid ($-COO^-$), phosphonic acid ($-PO_3H^-$), sulfonic acid ($-SO_3^-$), phosphoryl ($-PO_3^{2-}$), etc. On the other hand, AEM attracts positively charged groups such as secondary amine ($-NRH_2^+$), ammonium ($-NH_3^+$), tertiary amine ($-NR_2H^+$), and quaternary amine ($-NR_3^+$). EDs are commonly employed in batch mode process, but in large plants, it is done in continuous mode for maintaining constant flow and quality of water.

Maigret and Sabates first proposed concept of ED in 1890. They have made a unit to demineralize the sugar syrup, and carbon was used for the electrodes and permanganate paper was used as membrane. Then, the first artificial ion exchange membranes were made by W. Juda and W.A. McRay in 1950. The development of electrodialysis reversal concept (EDR) boosted the progress of the ED technology (Campione et al., 2018). The ED process is considered as a mature desalination process for over 50 years. Besides desalination, the other important operation performed by ED is nutrient recovery from the wastewater.

Khaoua et al. recovered ammonium from wastewater employing ED process. Ippersiel et al. were able to obtained 21.35 g/L NH_4^+-N from swine manure using ED in a batch mode process (Ippersiel et al., 2012; Khaoua et al., 2012). Moreover, ED can be employed to separate organic nitrogen from inorganic nitrogen and ionic nutrients from organic ones (Chon et al., 2013; Zhang, van der Bruggen, et al., 2009).

However, ED process has many drawbacks such as it is not suitable for very diluted solution, medium has high resistance, and energy consumption is very high. Some of these problems are eliminated by hybrid system of electrodialysis-based electrodeionization (EDI).

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3.3 Electrooxidation

Electrooxidation (EOx) is the process in which OH• radicals improve the treatment efficiency by increasing the reactivity for electrochemical mineralization of the organic compound. This process transfers the pollutants in the wastewater finally into harmless products such as CO_2 and H_2O (Martínez-Huitle and Ferro, 2006). Two main mechanisms of EOx process are:

- Direct oxidation by anodic electron transfer where pollutants are mineralized by OH• (Dirany et al., 2010).

$$M(H_2O) \rightarrow M(OH^{\bullet}) + H^+ + e^-$$

- Indirect oxidation with active chloride. This process takes place when chloride is present in the electrolyte (Murthy et al., 2007).

$$\textbf{Anode}: 2Cl^- \rightarrow Cl_2 + 2e^-$$

The efficiency of the treatment depends on the electrode material. Electrodes with high oxygen overvoltage (e.g., PbO_2, SnO_2) termed as nonactive electrodes perform well, on the other hand, those that have low oxygen overvoltage, i.e., active electrodes (e.g., Pt, IrO_2), perform much worse. In the nonactive electrodes, OH• radicals form with direct oxidation reaction. The OH• radicals remain physically absorbed to the surface of the anode and provide instability, reactivity, and a higher oxidative potential for the degradation of the organic maters to CO_2. The use of nonactive electrodes seems to be enough and the best option for the method. But corrosion of the electrodes takes place because of the generation of oxygen bubbles and high pressure on the electrode surface during this process (Moradi et al., 2020). The active anodes are more electrocatalytic and oxidize chloride to active chlorine species through indirect oxidation path. Treatment of saline wastewater can be done with this process. Bacteria and other organics can also be neutralized with this oxidation method.

3.4 Electrokinetic

Electrokinetic process is the effect of particle motion in an electric field. These are of many types such as electrophoresis, electromigration, electroosmosis, etc. Electrophoresis is the motion of charged particles through stationary liquid. Electromigration is the movement of ions due to their own mobility, which is a function of the electric charge, diffusion coefficient, and temperature. This can be treated as a type of electrophoresis, but in this case, the particle size is negligible. Electroosmosis is displacement of bulk water molecules at the interface of solid and liquid.

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In electrophoresis, the particles acquire surface charge from own intrinsic ionization or by adsorption of polyelectrolytes, surfactants, or ions onto their surface. As the surface area of the colloidal particles is large relative to the volume of the particles, the electronic repulsion overcomes the van der Waals interaction. Thus, particles are prevented from coagulation. When the electric field is applied through the colloidal solution, the charged particles move toward the electrode of opposite charge. The velocity of the particles increases with the field intensity. Electromigration is the process where the charged particles move because of the charge equilibrium imbalance imposed by exchange of electrons from electrode. In general, the ionic mobility is a function of concentration of ions. During the electrokinetic treatment, the concentrations in the system are changing, and thus, the conductivity changes also. To make the system of electroosmosis and electrophoresis work, the electrodes need to be in contact with the medium to ensure an electric field flow. This is carried out using an imposed voltage (or current) through an external power supply.

4. Application of electrochemical technologies

4.1 Pollutant and organic removal

The EC process is applied in treatment of various industrial wastewater. More than 90% of color and COD and around 87% of BOD removal are reported by Sridhar et al. (2011). Black liquor, one of the main pollutants of paper and pulp industry, can be treated by this method. Zaied and Bellakhal reposted 99% color, 98% COD, 92% polyphenols removal efficiency after treatment of black liquor by EC process (Zaied & Bellakhal, 2009). Studies on pharmaceutical wastewater treatment reported 99.89% TOC and 100% removal of metronidazole at controlled pH and current density (Orlowska et al., 2018; Veli et al., 2016). Tannery wastewater cannot be easily treated with biological method due to its high toxicity. EC process is employed for removing the TDS, COD, and chromium from the tannery wastewater. It was reported that using aluminum as cathode process has shown maximum removal efficiency of more than 90% removals of BOD_5, COD, turbidity, chromium, and iron (Benhadji et al., 2011).

Conventional ED and hybrid ED with various technologies such as air stripping and RO process were employed. Researches used hybrid ED and were able to increase the NH_4^+-N concentration from 3200 to 21,352 mg/L (Ippersiel et al., 2012). ED with RO was reported to increase NH_3-N concentration by three to five times (Mondor et al., 2008). High amount of K and NH_4^+-N was reported to be recovered from domestic wastewater by pilot-scale ED (Ward et al., 2018). Conventional ED was able to recover PO_4^{3-}-P and NH_4^+-N from urine solution containing micropollutants (Pronk et al., 2006).

The EC and EOx each have advantages and drawbacks, and either process alone cannot give completely effective removal or particle and industrial

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pollutants. But combining these two processes, a whole synergistic method to remove particle and mineralize organics in reasonably short time can be developed. EC can remove the particle in a very short time but not sufficiently able to remove the organic part of the wastewater. EOx very easily breaks down the organic part but requires much time and has limited applicability when colloidal and suspended particles are present. In the combined EC and EOx process, EC removes the particles, and some of the organic matters and the rest of the organic matter are removed by the EOx process. This coupled process eliminates COD, BOD_5, color, turbidity, and coliforms in a comparatively short amount of time, about 2 h. Removal efficiency in all types of electrodes was found to increase with increasing operating time. COD removal efficiencies using different electrode materials at 50 min operation time were found to be 97% for Ti/SbO_2-SS, 87.5% for Ti/SbO_2−CC, 81.2% for Ti/PbO_2-CC, and 73.3% Ti/PbO_2-SS. Ti/SbO_2 anode electrode, and stainless steel cathode system achieved the most effective removal efficiency (Özyonar and Korkmaz, 2022).

The flow-through EO process could remove up to 98% of NH_4^+-N, 96% of NO_2^--N, 72% of P, and 48% of COD. This process can also remove of antibiotics and sterilize with low amount of energy consumption of 0.27 kWh/m^3. This method is used with EC process.

To separate the particles from the fluid media, electrophoresis is used. Simultaneously with filtration process, electric field is used to move the particles away from the membrane and to resist the cake formation on the membrane. Electrophoresis is used to analyze accurately substances, such as your blood and DNA by separating DNA, RNA, or protein molecules based on their size and electrical charge using an electric current to move the molecules through a gel or other matrix.

4.2 Metal removal

Heavy metals are some of the harmful pollutants that have toxicity, carcinogenicity, nonbiodegradability, and long-term pollution capability in the environment. ED method has been tested to treat wastewater containing heavy metal. Among these heavy metal, Ni, Zn, Pb, Zn Cr, Fe separation was conducted by ED (Martí-Calatayud et al., 2018, p. 1566; Sharma & Shahi, 2020).

5. Bioelectrochemical system

Globally, significant sums of money are spent each year to treat enormous amounts of wastewater, which uses a tremendous amount of energy. Since the wastewater contains organic contaminants that can be converted into electricity, biohydrogen, and high-value compounds, the wastewater can be exploited as a renewable resource and help save a great deal of energy and

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money. This is possible if electroactive microorganisms in an electrochemical cell oxidize the organic component, which also aids in the treatment of wastewater. In BESs, which convert chemical energy into electrical energy, microbes serve as catalysts (Bajracharya et al., 2016). Due to rapid population growth and the advancement of industry and agriculture, fossil energy sources have been consumed rapidly in recent decades. The severity of environmental contamination has increased at the same time as new contaminants have emerged. The need of creating new, clean energy sources has increased due to the rising demand for fossil fuels and the desire to reduce environmental pollution (Cheng et al., 2009). BESs have drawn a lot of attention in the past decade decades due to its relevance as a developing sustainable technology for the concomitant production of power and wastewater treatment, as well as biogas and valuable chemicals (Venkata Mohan et al., 2010).

Low-energy wastewater treatment is achieved by BESs, which exploit the electron transport mechanism in biological organic decomposition to generate power directly from biowaste (Wang & Ren, 2013). Anodes and cathodes constitute the BES, which can generate energy or other chemicals (Fig. 6.2). In the anodic chamber, electrochemically active bacteria (EAB) oxidize organic materials, consequently transporting electrons to the anode. Under the influence of an external current, protons (H^+) formed during the catalytic conversion flow, through an ion exchange membrane from the anode chamber to cathode chamber, were employed in the synthesis of compounds with added value. Due to its potential uses in the domains of wastewater treatment, bioremediation, and other by-product reclamation, BES has drawn a lot of interest from researchers.

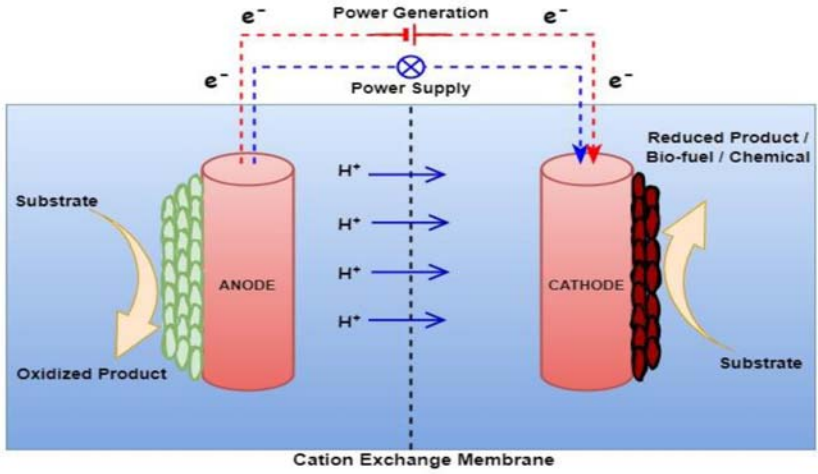

FIGURE 6.2 Diagram of a bioelectrochemical system.

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6. Types of bioelectrochemical system

BESs may typically be classified as microbial fuel cells (MFCs), microbial electrolysis cell (MEC), microbial electrosynthesis (MES), microbial solar cells (MSCs), and microbial desalination cells (MDCs) based on the projected outcome and intendent function (Bajracharya et al., 2016). Depending on the biocatalyst, BESs can be classified as either MFCs or enzymatic fuel cells (EFCs) (Osman et al., 2011). These systems are now referred to as MXC, with the X standing for the many types and applications (Pant et al., 2012). The next section discusses each type of BES. Fig. 6.3 shows different types of BES.

6.1 Microbial fuel cell

In MFCs, microorganisms use the microbial degradation of organic substrates to convert chemical energy into electricity (Lovley, 2006). In anaerobic anode compartments, certain bacteria oxidize organic compounds, creating protons and electrons in the process. In the absence of oxygen, these bacteria must transmit the electrons liberated during oxidizing organic materials to anode. The electrons are subsequently transported via an external wire to an electron acceptor, where they are reduced. As protons are produced at the anodic chamber, they are either transmitted by the electrolyte or across a membrane

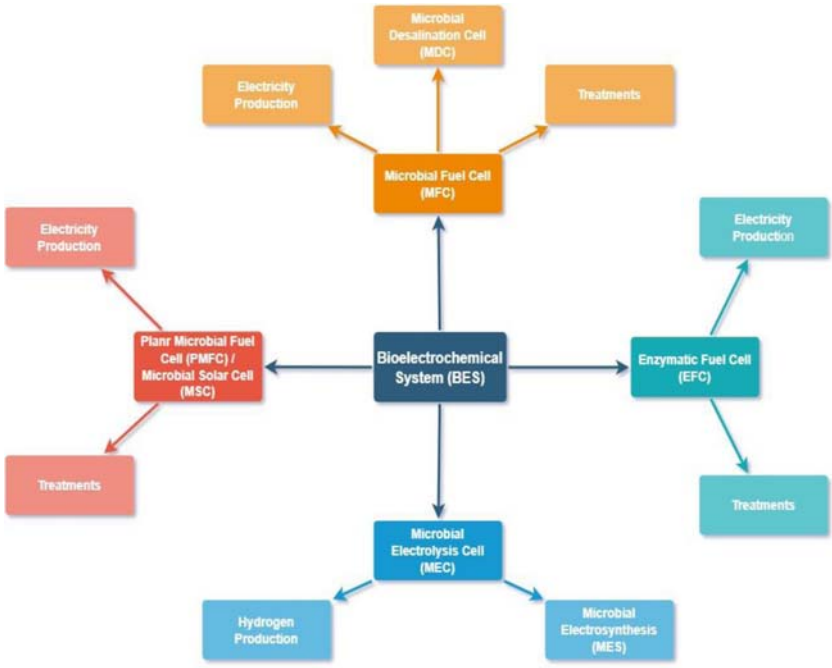

FIGURE 6.3 Types of bioelectrochemical system.

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dividing the cathode from the anode. Electron acceptor TEAs such as oxygen, sulfate, and nitrate have the potential to diffuse into the compartment and take up electrons to create new compounds that can be released. Some exoelectrogenic bacteria have the ability to transport their electrons to electron acceptor outside of the compartment. These microorganisms produce electricity in MFC systems. Most MFCs produce water when protons from the anode chamber cross the membrane and combine with oxygen and electrons that are transferred to the cathode. The earliest of these devices, which produced a voltage output of 0.3−0.5 V, was showed in 1991 by Potter (1911).

MFCs are often divided into two groups according on the process by which power is transmitted from bacteria to the anode. Depending on whether an external mediator is required, MFCs may be grouped into two categories: mediator MFCs and mediator-less MFCs. Synthetic mediators such as anthraquinone-2,6-disulfonate (AQDS) are incorporated to mediator MFC to enhance the flow of electrons from the microbes to the anode (Logan et al., 2006). In this kind of MFC, microorganisms are unable to transport electrons directly to the anode due to the nonconductive character of their cell surfaces. These MFCs can become more efficient at electron transfer by adding suitable external electron mediators. The MFC is referred to as a mediator-less MFC if there are no external mediators present. It is possible to characterize the mediator-less MFC according to the capacity of the bacteria to transport electrons from the microbial cell to the anode either directly or by self-synthesized electron shuttles. An organism that directly transfers electrons in a mediator-less MFC is called an "exoelectrogen" or an "electroactive bacteria" (EAB). Bioelectrochemically active bacteria are *Shewanella putrefaciens*, *Geobacter metallireducens*, etc.

In the reactor system, anodic substances must be conductive, chemically stable, and biocompatible. The most adaptable electrode material is carbon. Graphite, carbon paper, and carbon cloth are frequently used as electrode materials for anode (Logan et al., 2006). Due to its excellent performance, ferricyanide (K3[Fe(CN)6]) is often used in MFC as a cathode material (Park & Zeikus, 2003). Oxygen is the best acceptor of electron for an MFC since it has higher potential of oxidation, is readily available, accessible, and sustainable, and does not produce chemical waste (only water). The anode and cathode compartments of the majority of MFC systems must be divided using a CEM. The proton exchange membrane (PEM) is another name for the CEM. There are certain exceptions, including sediment MFCs and specially manufactured single-compartment MFCs. The most often employed CEM is nafion (Logan et al., 2006).

6.2 Microbial electrolysis cell

MECs are a form of microbial bioelectrochemical technology that uses electricity and was initially designed to produce biological biohydrogen from

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wastewater. A prospective technological advancement based on the mechanism of microbial electrohydrogenesis is the MEC system (Pandit et al., 2017, pp. 165−188). This technique addresses the problems of energy needs for the generation of H_2, treats sewage, and increases the supply of freshwater (Hua et al., 2019). It is a modified form of the MFC in which microorganisms known as exoelectrogens perform degradation of organic matter and deliver electrons to the anode. Unlike MEC systems, where the cathode is fully anaerobic and cannot produce any spontaneous current, the MFC system produces an electric current by the reduction of oxygen. A number of wastewaters, including sewage sludge, cellulose, glucose, glycerol, and acetic acid, may be turned to hydrogen in MECs. It is possible to produce hydrogen even from by-products of dark fermentation (like acetate) with excellent rates. When compared with conventional water electrolysis, which requires a high energy input (>2.1 V), the formation of hydrogen at the cathode is enabled by a minimal external current (0.2−0.8 V) that is delivered (Zhang & Angelidaki, 2014) A typical dual-chamber MEC comprises a cathode chamber, and an anode chamber, with a membrane dividing the two-electrode chambers and a power supply. Bipolar membranes, charge-mosaic membranes, AEMs, and CEMs are examples of separators. Exoelectrogenic strains colonize the anode to create a biofilm, which work as a biocatalyst to facilitate the anodic process. Electrons, protons, and carbon dioxide are produced by anodic biofilm by the biological oxidation of organic matter. Through an external electrical circuit, electrons travel to the cathode where they reduce H_2O and protons to form $OH-$ and $H+$. The MEC's cathode potential is greater than its anode potential, preventing spontaneous transmission of electrons from the anode to the cathode. As a result, it is important to include a low supply of power (0.2−0.8 V) to initiate the movement of electrons. In an MEC, a variety of organic materials, including acetic acid, glucose, cellulose and wastewater, can be converted into biogas. In addition to hydrogen, different chemicals such as methane (CH_4), formic acid (HCOOH), hydrogen peroxide (H_2O_2), etc. are produced (Hua et al., 2019).

The typical MEC system comprises of two chambers, where the cathode and anode chambers are separated by a slender ion exchange membrane and linked through an external wire. As contrary to this, the single-chambered MEC device was designed with the intention of cost reduction and optimizing the reactor architecture. Since oxygen is not formed in the cell, there is no reason to inhibit cathode gas from reaching the anode compartment. Comparing the two designs reveals that the single-chambered systems produce greater amount of hydrogen and higher density of current than the double-chambered devices. The benefits of a single-chamber membranes-less reactor include a reduction in potential loss and a decrease in the impact of pH loss. In contrast, in a double-chambered MEC, the membrane prohibits the back diffusion of hydrogen from the cathode chamber to the anode chamber, ensuring the purity of the Hydrogen gas. MEC with dual chambers has the disadvantage of having a large distance between electrodes, which leads to a

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substantial increase in system resistance, resulting in potential losses from the Ph gradient (Varanasi et al., 2018).

MECs capitalize on exoelectrogenic bacteria's unique capability to respire via the extracellular electron transport. Exoelectrogenic microorganisms can transfer electrons to the anode of an MEC by immediate contact with extremely conductive nanofibers, soluble electron shuttles, or membrane-associated proteins. Mixed cultures or actual wastewater has been used as inoculum for the majority of the MEC investigations that have been carried out. Due to greater degradation efficiency, mixed consortia have been shown to produce greater yields than pure cultures (Juang et al., 2011). Proteobacteria, which include *Geobacter sulfurreducens*, *Rhodoferax ferrireducens*, *Pseudomonas aeruginosa*, and others, make up the majority of the electrogens that are isolated from MECs. Besides these, reports have been published on microorganisms belonging to the group Firmicutes, acidobacteria, and actinobacteria (Varanasi et al., 2018).

There have been numerous potential applications of MECs, including synthesis of chemicals (e.g., biohydrogen, biomethane, formic acid, and hydrogen peroxide), removal of recalcitrant contaminants, and extraction of resources and biosensors. H_2 is a significant alternative to fossil fuels because of its properties, harmless, ecofriendly renewable energy source, and extremely combustible gas with a large calorific value of 142.9 kJ/g (Leicester et al., 2020). In the cathode compartment of MEC, hydrogen gas can be generated in one of two ways: either by reducing hydrogen or through reducing proton. Methanogenesis, which entails oxidizing hydrogen via methanogens in a community of anode biofilms, is an undesirable side effect that lowers the efficiency with which MECs produce hydrogen, particularly when a single-chambered MEC is used (Zhou et al., 2013). Direct generation of CH_4 in MEC has a number of benefits over conventional anaerobic digestion processes, including high CH_4 synthesis, high tolerant methanogens, and effluents with low concentrations of organic materials. The output of HCOOH was achieved via organic substances oxidation in the anodic chamber and CO_2 reduction in the cathode. The feasibility of H_2O_2 production is based on the microbial oxidation of organic waste in the anodic chamber combined with reduction of O_2 in the cathodic chamber of MEC (Hua et al., 2019). As a novel wastewater treatment technique, MEC technology has enormous potential. Organic contaminants such as nitrobenzene can be eliminated in MFCs. The feasibility of removal of BTH (benzothiazole) derivatives, chlorinated phenol contaminant (4-CP), and halogenated aromatic compounds using MECs is successfully investigated (Jiang et al., 2016; Liu, Ding, et al., 2016; Miran et al., 2017) The MEC can degrade a variety of inorganic pollutants, including nitrate, sulfur, perchlorate, and phosphorus (Cecconet et al., 2018; Li et al., 2015; Lin et al., 2018). In MECs, multiple metal treatments have been applied, such as silver recovery, ferric ion reduction, ferrous ion oxidation, copper removal, and recovery (Nancharaiah et al., 2015).

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6.3 Microbial electrosynthesis

Microbial electrosynthesis (MES), often referred to as bioelectrosynthesis, is driven by electricity and involves microorganisms taking electrons from the cathode and reducing carbon wastes such as CO_2 to value-added chemicals (Jourdin & Burdyny, 2021). An MES typically comprises a cathodic chamber and an anodic chamber divided by a PEM. Biotic anodic chamber and AEM and CEM have been employed in MES research (Xiang et al., 2017). In the anodic compartment, water splits to produce protons, electrons, and oxygen; then protons are transported to the cathodic chamber through the PEM, electrons through an external circuit and oxygen are liberated into the environment (Das et al., 2018). An external potential is applied using a potentiostat to draw electrons from the anodic chamber to the cathodic chamber. As protons and electrons are transferred from the anodic chamber to the cathodic chamber, they react with CO_2, which is supplied as feed, when there was microorganisms functioning as a biocatalyst to synthesize several valuable organic chemicals (Das et al., 2021). The crucial elements of microbial electrosynthesis are biocathodes, which enable the microorganisms to produce value-added products such as ethanol, acetate, and butyrate (Bajracharya et al., 2015).

Nevin et al. demonstrated in 2010 that extracellular multicarbon compounds could be produced microbially from carbon dioxide and water by supplying electrons to the homoacetogen *Sporomusa ovata* growing at the cathode of a BES (Nevin et al., 2010). CO_2 reduction in products has drawn the most attention as it is seen as a more viable route than traditional fermentative routes (Rabaey et al., 2011). The homoacetogenic microorganisms that execute out the Wood-Ljungdahl pathway is responsible for MES from CO_2 (Ragsdale & Pierce, 2008). Because it combines endergonic reactions with other exergonic processes that do not require ATP, this carbon fixation pathway is the most energy-efficient (Rabaey & Rozendal, 2010). Carbon is assimilated in the form of ethanol, butanol, acetic acid, butyric acid, etc.

It has been more than a decade since the first proof-of-concept, microbial CO_2 reduction has been achieved on a cathode. MES research focused on the development of cathode materials, enrichment of microbial catalysts and electroactive microorganisms, improvement of productivity and selectivity, and providing insight into microbial functions and mechanisms of extracellular electron transfer.

6.4 Microbial desalination cell

The MDC is a relatively new technology that combines the MFC process with electrodialysis for the treatment of effluents, desalination, and the electricity generation. The MDC technology is a further development of MFC

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technology. The MFC unit consists of two electrode, an ion-selective membrane, and an external circuit. The anode continues to operate under an anaerobic environment, while the cathode operates under an aerobic one. MFC can function with or without the assistance of a mediator; mediated fuel cells oxidize the substrate by introducing additional microorganisms (Saeed et al., 2015). Cao reported the first MFC-based water desalination technology in 2009 (Cao et al., 2009). MDCs have a separate middle compartment for the desalination of water, located in the center of the cathode and anode compartments. A CEM is placed in the cathode direction. In contrast, an AEM is placed in the direction of the anode in the intermediate compartment. In the anodic chamber, electrochemically active bacteria oxidize biodegradable organic matter, consequently producing electrons and protons. The electrons are sent to the cathode via an external circuit. To maintain charge neutrality, anions (e.g., Cl^- and SO_4^{2-}) migrate to the anode and cations (e.g., Na^+, K^+, Ca^{2+}) migrate to the cathode, thus desalinating the middle chamber solution (Luo et al., 2011, 2012). Usually, O_2 is the electron acceptor in the cathode chamber. Utilize these electrons for a reduction to make water. This technique is capable of removing greater than 99% of the salt that is present in brackish water and yet simultaneously producing enough power than the amount of additional electricity that is necessary for the system to function (Forrestal et al., 2012). The desalination rate (DR), which is highly reliant on the salt concentration of the seawater, is one of the most crucial performance metrics for MDCs. In general, MDC is seen suited for desalination of concentrated seawater, as the increased salt content may decrease the ohmic resistance in the MDC, leading to a high density of current across the circuit. Desalination performance may also be affected by the salt concentration gradient between the two electrode chambers and the intermediate desalination chamber (Yuan et al., 2012).

Existing MDC configurations are three-chamber cubic design, air cathode and biocathode MDC, recirculation MDC, stack structure MDC, submerged microbial desalination−denitrification cell, separator-coupled stacked circulation MDC, ion exchange resin−coupled MDC, capacitive MDC, up-flow MDC, osmotic MDC, bipolar membrane MDC, decoupled MDC (Saeed et al., 2015). The MDC can be used to remove salt and organic material while also making electricity, or it could perhaps be added with traditional reverse osmosis (RO) system like a pretreatment to reduce the salt concentration of the feed water and use less electricity (Bajracharya et al., 2016). In addition to treating wastewater, the submerged microbial desalination denitrification cell (SMDDC) was developed for nitrate removal. To reduce the energy consumption of the water softening process, an enzymatic method of MDC was devised. The MEDC can desalinate seawater and generate hydrogen at the same time. The recovery of ammonia, sulfate, and volatile fatty acids are only a few of the new applications for modified MDCs (Carmalin Sophia et al., 2016).

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6.5 Enzymatic fuel cell

EFCs employ certain enzymes on the electrode surface (or in an electrolyte solution) to promote the oxidation of fuel and drive particular processes that are favored for a variety of uses. EFCs are bioelectronic systems that convert energy into electricity by oxidizing organic compounds and/or reducing oxygen or peroxide using oxidoreductase enzymes as electrocatalysts. MFCs employ entire microbes with whole enzymatic pathways, whereas EFCs use certain distinct enzymes. As a result, whereas enzymes are specific, to substrate, microorganisms frequently work together and can produce a variety of biofuels. The most common enzymes responsible for electron transfer reactions are oxidoreductases. Different subclasses of oxidoreductases are defined by the substrate usage and the mechanism of reaction (peroxidases, dehydrogenases, oxidases, and so on) (Barelli et al., 2019). Enzymes are biological catalysts that are used in EFCs to oxidize fuel at anode and reduce oxidants at cathode. In contrast to conventional fuel cells, the right choice of enzyme enables these reactions to take place in relatively benign conditions (neutral pH, ambient temperature). Glucose biofuel cells (GFCs) are a type of EFCs that effectively turn glucose and oxygen into electricity by breaking them down with enzymes. Redox enzymes comprise of an apoenzyme (protein constituent of an enzyme) and one or more cofactors (tiny electroactive nonproteinaceous species). The cofactor ensures that the enzyme transfers electrons to the substrate or cosubstrate. During the reaction, the cofactor can either be strongly linked to the enzyme or released from the active site. There are several common cofactors for enzymes that oxidize glucose, including nicotinamide adenine dinucleotide (NAD), flavin adenine dinucleotide (FAD), and pyrroloquinoline quinone (PQQ). Due to their high sensitivity of glucose and greater density of current, the flavin adenine dinucleotide-dependent glucose dehydrogenases (FADGDH) or osmium (Os) polymer-based electrodes are appropriate for use as bioanodes in glucose-based EFCs (Zafar et al., 2012). To improve the system's overall performance and substrate conversion, EFCs based on multienzyme are typically favored to monoenzyme systems. Studies are increasingly concentrating on three-dimensional electrode architectures to offer plenty of contact area for enzymatic reactions and cascades of enzymes to enable complex processes.

6.6 Microbial solar cell

MSC is a recent invention that uses sunlight to generate energy or chemicals such as hydrogen, ethanol, methene, hydrogen peroxide, etc. In MSCs, photoautotrophic microbes or higher plants are utilized to harness solar energy, while microorganisms that are active electrochemically are used to generate an electrical current in the BES. At the anode of the MFC, electrochemically active bacteria oxidize organic compounds and transport electrons to anode. Through an energy harvester, these electrons are sent to the cathode, where

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they decrease oxygen. MSC's photosynthetic organisms use solar light to generate organic substances, which the MFC subsequently transforms into energy (Strik et al., 2011). According on MSC principles, a method for treating algal blooms in lake was published. This method involved feeding lake water and algal material from *Microcystis aeruginosa* and *Chlorella vulgaris* into MFCs to produce energy and potable water at the same time (Wang et al., 2012). The average power density of an MSC with a photobioreactor containing *Chlorella* at anode was 14 mW/m^2, with electricity from sunlight conversion efficiency of 0.04% (Strik et al., 2011). Performance can be enhanced by optimizing the photobioreactor, enhancing the chemical energy transmission from the algae to the bioanode, improving the surface area of electrode, and enhancing the biofilm that is electroactive.

6.7 Plant microbial fuel cell

Plant microbial fuel cells (PMFCs) are MSCs that contain higher, living plants. In PMFCs, plant roots excrete rhizodeposits that fuel electrochemically active microbes at anode. The excretion of organic compounds by plant roots into the soil is known as rhizodeposition and includes compounds such as sugars, organic acids, enzymes, and dead cell matter. About 20%−40% of a plant's photosynthetic productivity occurs in the rhizodeposits, and a mixture of microorganisms can degrade these compounds (Lynch & de Leij, 2012). According to the first PMFC study that was published, under the climatic conditions of Western Europe (specifically, the Netherlands, Belgium, and France), a net power generation of 67 mW/m^2 is theoretically feasible (Strik et al., 2008). The selection of a plant for PMFC is vital because it directly affects the quantity of rhizodeposits needed to produce energy. *Pennisetum setaceum* PMFCs have been described as the most reliable energy generator to date, with a highest power production of 163 mW/m^2 (Chiranjeevi et al., 2012). PMFCs and MSCs with phototrophic biofilms are regarded as innovative and promising energy harvesting process. Additionally, it was found that bioelectricity generation directly correlates with the net amount of rhizodeposits accessible for oxidation at anodes rather than the plant's photosynthesis process.

7. Applications of BES

BESs are mostly used to generate power or chemicals. The BES technology also offers several other advantages.

7.1 Wastewater treatment

Among the most important uses for BES is in wastewater treatment. Conventional technologies that use a lot of energy and are not good for the

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environment are currently used for the biological treatment of low-concentration wastewater. The best method for offsetting the enormous amount of energy used in conventional wastewater treatment is to use new methods that allow for significant energy recovery. A conventional municipal wastewater treatment plant that uses aerobic activated sludge treatment and anaerobic sludge digestion need 0.6 kWh/m^3 of treated wastewater. About half of this energy is used for aeration purposes (McCarty et al., 2011). Anaerobic conversion of organic components to methane allows energy recovery from domestic wastewaters. Membrane bioreactors can provide efficient treatment and great water quality, but they require a lot of energy (one to two kWh/m^3). Although anaerobic digestion has the potential to replace activated sludge as the primary treatment method, it is only effective in very large digesters and requires highly concentrated wastewater (>3 kg organic matter per m^3) and higher temperatures (>20°C). Because of these things, anaerobic digesters have only been used to treat sludge in conventional treatment plants (Logan & Rabaey, 2012). Maximum power densities of 12 W/m^3 have been achieved in MFCs using only domestic wastewater and no other energy source (Hays et al., 2011). Since that domestic wastewater contains 2 kWh/m^3, this energy recovery is minimal.

A projection of the economic benefit of scaling-up MFCs for wastewater treatment revealed that energy production will not be sufficient to justify MFC technique, but organic waste degradation is much appealing with this more eco-friendly technology. Real wastewater (e.g., municipal and brewery wastewater) as well as synthetic wastewater, such as sucrose, glucose, and acetate, have both been used to run MFC. Chemical oxygen demand (COD) concentration in the effluent can be decreased analogously by removing electrons from the anodic chamber (Fornero et al., 2010). According to Min and Logan, a lab-scale MFC with a hydraulic retention time (HRT) of 1.1 h and a 42% removal efficiency of COD was able to continuously produce energy at a rate of 72 mW/m^2 (per surface area of anode) from wastewater (Min & Logan, 2004). Rabaey et al. observed a maximum density was power of 3.6 W/m^2 and a coulomb efficiency of 89% in a batch MFC supplied with glucose at a rate of 2000 mg/L (Rabaey et al., 2003). Acetate, glucose, municipal wastewater, and hospital wastewater were all used in experiments with a continuously fed tubular MFC with an external cathode. For these effluents, the highest power outputs were 48 (20 Ω resistance), 35 (20 Ω), 10 (75 Ω), and 25 (Ω not stated) W/m^3 at COD concentrations of 458, 467, 429, and 332 mg/L and coulomb efficiencies of 98%, 74%, 20%, and 36%, respectively (Rabaey et al., 2005). Using bioelectrochemically aided microbial reactors (BEAMRs), the synthesis of hydrogen from domestic wastewater was investigated; this indicates the high treatment efficacy of the MEC system, as 97 ± 2% of biochemical oxygen demand (BOD), 95 ± 2% of chemical oxygen demand (COD), and 92 ± 2% of dissolved organic carbon (DOC) were eliminated in 432, 540, and 270 h, respectively (Ditzig et al., 2007).

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7.2 Production of chemicals

Large volumes of dissolved organic matter are present in wastewaters from industrial, agricultural, and municipal sources and could be used as a resource in the production of chemicals and fuels. Biological treatments produce energy from wastewater. Biogas is produced worldwide through methanogenic anaerobic digestion (a methane−carbon dioxide blend). Acetogenic fermentation produces biohydrogen from wastewaters (Venkata Mohan et al., 2009). BESs can be used to generate fuels and chemicals such as hydrogen peroxide, hydrogen, methane, and ethanol. Compared with conventional water electrolysis, BESs offer an alternate approach for increasing hydrogen yield with a comparatively low electric energy input. This technology is also termed bioelectrohydrogenesis. MEC studies have used mainly raw organic sewage as their substrate; therefore, the production of H_2 has been low and the production of CH_4 has been high (Li et al., 2017). Table 6.2 lists research on H_2 production in MECs fed with fermentation effluent. Future applications of MECs face a significant hurdle in the modification of cathode catalysts for the production of H_2. An ideal cathode catalyst material has to be inexpensive, easily fabricatable, robust under challenging conditions, and catalytically active. NiW and NiMo codeposits were examined as MEC cathodes, and Mitov et al. found that cathodic H_2 recovery of 79% and 89% were produced at 0.6 V applied voltage (Mitov et al., 2017). To create hydrogen in a microbially catalyzed bioanode, Cai et al. designed a 3D biphasic Ni5P4-NiP2 nanostructure. They were successful in doing so by producing hydrogen at a high rate of 9.78 mL/day cm^2 (Cai et al., 2018). Scalable reactors with high density of current, low internal resistance, and high recovery of hydrogen are necessary for the practical deployment of an MEC for hydrogen generation. Guo et al. constructed a tubular MEC on a liter scale, and the reactor's low internal resistance allowed it to produce hydrogen at a rate of 7.1 L/L day at a voltage of 1 V with an approximately 100% hydrogen recovery (Guo et al., 2017). In MEC technology, the main challenge is to enhance the rate of H_2 production with low energy input (Hua et al., 2019).

Methanogens are often seen in MECs that produce H_2. Hydrogenotrophic methanogens such as Methanobacterium and Methanobrevibacter, which can use hydrogen for their development and so reduce H_2 generation, predominate on the cathode. Direct generation of methane in MECs has a number of benefits over conventional anaerobic digestion processes, including high production of methene, high tolerant methanogens, and effluents with low levels of organic substances. Anode respiring bacteria (ARB) demonstrated an advantage over methanogens, which are acetoclastic in methene-generating MEC reactor for prolonged HRTs. The development of viable, cost-effective cathode materials that are both biocompatible and efficient is one of the main obstacles to CH_4 production in MECs (Hua et al., 2019). In the study using heat-treated stainless steel felt as a biocathode, Liu et al. found that

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TABLE 6.2 H_2 production in MEC.

Reactor	Substrate	Applied voltage (V)	Coulombic efficiency (%)	Maximum H_2 Production rate (m^3/m^3 day)	References
Single chamber	Dewatered sludge	0.9	78.89	0.038	Hu et al. (2018)
MEC stack	Urban wastewater	1.5	28.00	0.032	Baeza et al. (2017)
Dual chamber	Synthetic wastewater	1.2	21.00	0.220	Almatouq and Babatunde (2017)
Pilot-scale MEC	Domestic wastewater	0.6	55	0.015	Heidrich et al. (2013)
Single chamber	Milk	0.8	50	0.086	Montpart et al. (2015)

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at cathode potentials of 1.3 V, it increased efficiency of current-to-methene to 60.8% and energy efficiency to 21.9% (Liu et al., 2017). The optimization of external energy may play a significant and vital role in the production of the methene. Numerous research have shown that combining MEC and anaerobic digestion might improve the conversion of organics into biogas. Table 6.3 lists research on the CH_4 production rate for MEC. In scalability tests on MEC with multielectrode setups for H_2 synthesis utilizing acetate as substrate, Rader et al. found that methanogenesis rates steadily increased with time. The system generated CH_4 with a high substrate conversion efficiency after 16 days of operation, indicating that electromethanogenesis took over as the primary process at the biocathode when fed effluent from dark fermentation and anaerobic digestion processes (Rader & Logan, 2010). When combined with an abiotic graphite anode, a biocathode dominated by *Methanobacterium palustre* has been shown to effectively produce methane from CO_2 by a mediator-less method (Cheng et al., 2009).

Electrochemical reduction of CO_2 to HCOOH has received attention as a technically and economically viable technology for valuable chemical production. Organic matter oxidation in the anode and CO_2 reduction in the cathode led to the production of HCOOH. Using this technology, carbon dioxide emitted during wastewater or waste treatment will be recovered and recycled without energy input, thus reducing greenhouse gas emissions (Hua et al., 2019). Wang et al. designed an MEC reactor with a two-layer rolled Sn-loaded gas diffusion electrode that achieved a maximum Faraday efficiency of $40.09 \pm 3.91\%$ and a production yield of 0.06 ± 0.006 mol/m^2 (Wang et al., 2015) According to

TABLE 6.3 CH_4 **production rate for MEC with different substrates.**

Reactor	Substrate	Applied voltage (V)	Maximum CH_4 Production rate	References
MEC-AD	Pig slurry	0.8	79 L/m^3 day^{-1}	Cerrillo et al. (2018)
MEC-AD	Waste activated sludge	0.8	91.8 g/m^3 day^{-1}	Liu et al. (2016b)
MEC AD	Waste food	0.3	12.1 ± 2.2 L day^{-1}	Park et al. (2018)
Up-flow MEC	Beer wastewater	0.8	367 mL/L day^{-1}	Sangeetha et al. (2016)
Three chambers	Anaerobic sludge	1.3	8.8 L/m^2 day^{-1}	Liu et al. (2017)

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Zhao et al. CO_2 can be converted into HCOOH at a production rate of up to 21 ± 0.2 mg/L h in a single MFC with a layer-by-layer self-assembly carbon nanotube/cobalt phthalocyanine−modified electrode (Zhao et al., 2012). Given its viability and relative environmental friendliness, an MEC-based production route could potentially replace the current fossil fuel−based production technique.

Electricity-driven reduction reactions were employed by MES to fix CO_2 in multicarbon compounds such as liquid fuels or chemicals containing multiple carbon atoms. This application is considered a technology for accumulating electrical energy in the carbone−carbon bond of chemicals with added value. Nevin et al. shed light on the fact of microbial electrosynthesis using the acetogen *Sporomusa ovata*, which could use electrons directly derived from a graphite cathode for the reduction of CO_2 to produce acetate and small amounts of 2-oxobutyrate (Nevin et al., 2010). Biological acetate reduction with hydrogen is a possible way to make ethanol from wet biomass waste. In these products, more than 85% of the electrons transferred at the cathodes were recovered. Subsequent research demonstrated the CO_2 reduction process using MES with a broader range of microorganisms. Other acetogenic bacteria, including *Sporomusa silvacetica*, *Sporomusa sphaeroides*, *Clostridium ljungdahlii*, *Clostridium aceticum*, and *Moorella thermoacetica*, were capable of reducing CO_2 to acetate, 2-oxobutyrate, and formate, according to these studies (Nevin et al., 2011). In the cathode compartment of a BES, acetate has recently been reduced to ethanol with the use of methyl viologen (MV) as a mediator. A maximum current density of 1.32 A/m^2 was recorded at pH 6 and a cathode potential of 0.55 V versus NHE. Under the applied conditions (pH 6, 40 mM acetate, 0.1 mM ethanol), the theoretical potential for acetate to ethanol reduction is −0.28 V. Thus, the cathode overpotential in their BES was −0.27 V. The maximum cathodic ethanol recovery was 49%, resulting in an ethanol production rate of 0.656 mmol/m^3 reactor day (Steinbusch et al., 2010). The production of H_2O_2 as a valuable chemical by MEC was found to be feasible. H_2O_2 has long been recognized as an environmentally friendly chemical. Waheed et al. used the MEC reactor to biodegrade recalcitrant chlorinated phenol and produce H_2O_2. The highest concentration of H_2O_2 (13.3 g/L m^2) was produced in this particular instance with an external voltage of 0.4 V (Miran et al., 2017). A small external voltage must be added to the MEC system to improve the rate and production of H_2O_2. The cathode potential has been identified as a critical parameter in the MEC for H_2O_2 production.

7.3 Nutrient and metal removal

Recovery of metals present in waste streams is necessary to reduce environmental impact and reuse finite resources. Nitrogen is a major nutrient used in fertilizers. The Haber-Bosch process is now used for commercial production,

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which requires a lot of energy (Hua et al., 2019). Kuntke et al. successfully recovered ammonium (NH_4^+) from urine (Kuntke et al., 2012). Ammonia recovery from wastewater using a MEC has been used recently. However, the separation of recovered ammonia from the MEC catholyte requires significant energy input in the form of solution mixing or gas stripping (Hua et al., 2019). A two-chambered MEC's bioanode compartment was coupled in series with a thermophilic lab-scale AD that was fed with pig slurry by Cerrillo et al. The outcome revealed that the MEC's anode compartment removed 14.46 g $N-NH_4^+/m^2$ of ammonium per day (Cerrillo et al., 2018). An MEC has the ability and the potential to recover phosphorus. Abdullah et al. studied P recovery in a dual-chamber MEC and observed that the maximum P precipitation efficiency was 95% when H_2 production occurred simultaneously (Almatouq & Babatunde, 2017).

MFCs have also been used to remove and recover metals from mining and metallurgical process leachates and effluents. In MECs, multiple metal treatments have been applied, such as uranium recovery, silver recovery, chromium reduction, ferric ion reduction, ferrous ion oxidation, cadmium (II) removal, mercury removal, and copper removal and recovery. Heijne et al. observed that copper could be reduced electrochemically at the cathode by oxidizing acetate bioelectrochemically at the anode (ter Heijne et al., 2010). Zhang et al. corroborated vanadium (V) and chromium (Cr) recovery in dual-chambered MFCs (Zhang et al., 2012).

7.4 Recalcitrant pollutant degradation

Recalcitrant wastes, such as dyes, pesticides, explosives, heavy metals, polyalcohols, furan derivatives, and phenolic substances, are of particular concern due to their recalcitrance and persistence in the environment. BESs, such as MECs and MFCs, combine three key wastewater treatment options—biologic treatment, electrolytic dissociation, and electrochemical oxidation/reduction—and are regarded as a new, efficient, and sustainable method of handling these wastes (Huang et al., 2011). Because of its higher degradation efficiency, low maintenance cost, and high environmental sustainability, MEC technology has significant potential as a new wastewater treatment technology, which is important for economical and efficient scale-up of the operation. Organic pollutants such as nitrobenzene can be removed in MFCs, but removal can be significantly enhanced in MECs with a limited energy supply. The feasibility of removing BTH derivatives using MECs, which are toxic and difficult to degrade xenobiotic heterocyclic chemicals, is being investigated. Chlorinated phenol pollutant 44-CP treated in a sulfate-reducing bacteria enriched MEC system that shows it removed 4-CP well and further degradation of dechlorinated substances. The combination of MEC and biological treatment has been successfully applied to reduce halogenated aromatic compounds such as 2,4-dinitrochlorobenzene, p-fluoronitrobenzene

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and p-nitrophenol (Hua et al., 2019). Table 6.4 illustrates the following recalcitrant substances that have been treated by BESs.

Many inorganic pollutant substances such as nitrate, perchlorate, phosphorus, and sulfur can be degraded in the MEC. In an MEC, nitrate is used as an electron acceptor at a bacteria-catalyzed cathode. The use of external voltage improved the generation of electric current and consequently reduced nitrates. There are several challenges for the MEC for nitrogen removals, such as system scalability, microbiological process, long-term operational stability, capital investment, operational cost, and economic and environmental evaluation. Bioelectrochemical sulfate reduction enhancement has been shown to significantly improve organic decomposition in the MEC. Dong et al. used a single-chamber MEC at 0.7 V with 600 mg/L potassium sulfide concentrations, and the sulfide removal rate reached 80.7%, with Geobacter as the dominant bacteria detected (7.35%) (Dong et al., 2017). Exploring the optimal operating conditions in real wastewater is one of the challenges of using an MEC for sulfate removal.

7.5 Biosensor

The testing of the quality of the water can be done quickly and easily using MFC technology. Recent studies have proposed MFC-based biosensors for the detection of toxic compounds and the measurement of biochemical oxygen demand (BOD) in water samples. For on-site and real-time water quality monitoring, MFCs may be advantageous. Because MFC technology can be constructed from inexpensive carbon-based materials, it can also be significantly more affordable than conventional sensors. To improve accuracy and expand the detection range to 130 mg-COD/L, Yuan et al. created MEC-based bioanode sensors (Yuan & Kim, 2017). However, there are several challenges associated with practical applications of bioanode sensors for evaluating water quality, including narrow detection range and long analysis times. Kim et al. made the first demonstration of MFC-based toxicity sensors, demonstrating how electrical current changed in response to the presence of contaminants such as heavy metals such as Pb and Hg, and organophosphorus pesticides (like Diazinon), and polychlorinated biphenyls (PCBs) in the water samples. Kim et al. show that the lowest detection limit of the MFC biosensors was 1 mg/L for heavy metals such as Pb, Hg, and Cr (Kim et al., 2007). In MFC biosensors, the rate of substrate consumption and microbial activity is primarily related to the electric current produced. When all other operational parameters remain constant and a toxin is present, there is a decrease in electric current, which indicates toxic inhibition. MEC has the potential to be a novel, portable bioelectrochemical BOD sensor that is more accurate. The long-term stability and durability of MEC sensors are a major hindrance to their practical application. Optimizing operating conditions and achieving MECs as real-time, in situ, and self-sustaining monitoring tools should be the focus of studies.

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TABLE 6.4 Recalcitrant substances treated by BESs.

Recalcitrant substance	Reactor	Electrode	Operating condition	Removal rate (mol/m^3 d)	Power output (MFCs)[a]/ Consumed (MECs)[b,c]	References
Nitrobenzene	Two-chamber MFC, acetate in anode, nitrobenzene in abiotic cathode	Granule graphite anode and cathode	Both anolyteand catholyte were recirculated and continuously fed	1.3	0.06[a]	Mu et al. (2009)
Nitrobenzene	Two-chamber MEC, acetate in anode, nitrobenzene in abiotic cathode	Granule graphite anode and cathode	Both anolyte and catholyte were recirculated and continuously fed	8.6	0.049[b]	Mu et al. (2009)
Pyridine	Two-chamber MFC, pyridine, and glucose in anode, ferricyanide in cathode	Graphite granule anode and cathode	Batch fed	10.3	48.5[a]	Zhang, Li, et al. (2009)
Pyridine	Two-chamber MFC, pyridine in anode, derricyanide in cathode	Graphite granule anode and cathode	Batch fed	15.0	1.7[a]	Zhang, Li, et al. (2009)
2-Chlorophenol	Two-chamber MEC, acetate in anode, 2-chlorophenol in biocathode	Graphite granule anode and cathode	Batch fed	0.04	−0.3[c]	Strycharz et al. (2010)

Continued

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TABLE 6.4 Recalcitrant substances treated by BESs.—cont'd

Recalcitrant substance	Reactor	Electrode	Operating condition	Removal rate (mol/m^3 d)	Power output (MFCs)[a]/ Consumed (MECs)[b,c]	References
4-Chlorophenol	Two-chamber MFC, acetate in anode, 4-chlorophenol in abiotic cathode	Carbon fiber anode and cathode	Batch fed	0.3	0.12[a]	Gu et al. (2007)
Trichloroethene	Added methyl viologen as a mediator	Glassy carbon cathode, platinum disk anode	Batch fed	0.001	−0.5[c]	Aulenta et al. (2007)
1,2-Dichloroethane	Two-chamber MFC, 1,2-dichloroethane in anode, ferricyanide in cathode	Graphite plate anode and graphite granule cathode	Batch cathode and recirculated anode	0.061 −0.068	5.3−15.2[a]	Pham et al. (2009)
Congo red	Two-chamber MFC, aerobic biocathode, glucose as cosubstrate	Carbon felt anode and graphite granular cathode	Effluent of the anode was looped to cathode	0.32−0.43	1.74−2.72[a]	Li et al. (2010)
Cr(VI)	Two-chamber MFC, acetate in anode, Cr(VI) in biocathode	Graphite plate anode and cathode	Batch fed	0.2	0.9[a]	Tandukar et al. (2009)

[a]*Power output calculated based on the net cathodic compartment (W/m^3).*
[b]*Power consumption of MECs calculated based on the net cathodic compartment (kWh/mol substrate).*
[c]*Potential via standard hydrogen electrode (V).*

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8. Advantages and drawbacks

Some of the main advantages are easy of operation, low cost of material, efficient removal of the targeted pollutants, recovery of valuable waste products, recovery of water, ability to treat colored wastewater and emerging contaminants, etc. One of the major drawbacks is production of high volume of sludge or production of high strength concentrate wastewater. Electricity supply is mandatory for these types of treatments; moreover, equipment for controlling operation and skilled manpower is required. Electricity-assisted processes depend on the voltage applied, and the time and efficiency are proportional to it. Some of the electrochemical methods use membrane as AEM or CEM that can increase the initial cost of the process.

The key benefits of BES are that it is environmentally beneficial (because to its minimal CO_2 emission), produces energy, is a fuel alternative, and can recover valuable chemicals and nutrients. The primary barrier to biofuel cell development is their low power densities or the amount of power produced per unit of electrode surface area. This is because of a number of significant obstacles, including sluggish transport through cell membranes. Ohmic voltage losses, which result from resistance to charge transfer and include both ionic and electronic resistances, concentration overpotentials, activation overpotential, and coulombic losses, are also significant losses in these systems. The factors hindering the commercial application of BESs include pH problems, high ohmic cell resistance, and high overpotentials. Upscaling is a significant obstacle that these systems must overcome. The difficulty and importance of the scale-up barrier are well acknowledged (Pant et al., 2012). Temperature has an impact on MFC performance as well since microorganisms cannot function and thrive in temperatures that are too high or low. MFC must be performed at a temperature that is ideal for microorganisms. Accordingly, to increase efficiency and improve the conductivity of electrons, researchers have been looking for a replacement. or new materials to use in the manufacture of the key MFC components, such as the cathode, anode, and membrane separator.

9. Conclusion

The wastewater treatment is an age-old practice but, with chronological development of various technologies, wastewater treatment is modified to become more efficient and to treat much boarder variety of pollutants. The incorporation of electricity to actively treat wastewater was conceptualized about two centuries ago and also became a reality some decades after that. Electrochemical treatments reduced the plant footprint and cost of the process. But, in modern times, the volume and characteristics of wastewater have changed. Besides, the idea of recovering value-added products from the waste is trending now-a-days. Therefore, ways for production of electricity and other

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energy-induced products have been rigorously studied by the researchers. The MFC and MEC are such systems that can harness energy from the wastewater. There is additional application of such technologies such as using it as biosensor that is self-powered. There is not many large-scale applications of such energy-harvesting wastewater treatment systems. But the progress of research is promising, and these processes have high potential to solve the energy problems that world will meet in near future.

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Chapter 7

Microbial electrosynthesis for synthesis of volatile fatty acids and industrial chemicals from wastewater

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Abstract

The chapter shall focus on microbe-assisted electrosynthesis of volatile fatty acids and other chemicals from wastewater. A brief introduction of microbial electrosynthesis shall be covered with emphasis on microbial electron transfer pathways for synthesis of reduced compounds. Various types of wastewaters used as substrate for energy recovery and different routes for product synthesis shall be covered. Genetically enhanced microbial systems for harvesting optimum energy from wastewater or synthesis of novel products by electrosynthesis shall be explored. Future perspective of microbial electrosynthesis for synthesis of industrially important chemicals shall be included.

Keywords

Metabolic pathways; Microbial electrosynthesis cell; Resource recovery; Value-added chemicals; Wastewater.

1. Introduction

Sustainable solutions for wastewater treatment, disposal, and reuse are becoming an urgent need for maintaining environmental balance. Several technologies such as anaerobic digestion, filtration, and membrane-based reactors have been implemented for harvesting energy, fertilizer, or resource recovery from wastewater. Bioelectrochemical systems (BESs) are microbial catalyst-based novel technologies for harvesting energy, waste valorization,

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and product synthesis from wastewater that is yet to be scaled up for commercial implementation (Jadhav, Chendake, et al., 2022; Jadhav, Park, et al., 2022). Major classes of BES include (1) microbial fuel cell (MFC) for harvesting electrical energy from chemical energy stored in wastewater; and (2) microbial electrosynthesis cell (MESC) for electrochemically producing reduced chemical compounds using wastewater substrate. As shown in Fig. 7.1, in a typical MESC, anodic electrogenic microbes produce electrons from substrate oxidation, which travels through an external circuit toward cathode where electrotrophic microbes incorporate these electrons and additional electrons from external power source to produce reduced compounds. Both the compartments are separated internally using a cation exchange membrane to assist proton diffusion from anode toward cathode. Abiotic reactions may be favored in either of the compartment as per the electrochemical requirement of the product synthesis (Quraishi et al., 2021). Most commonly produced chemicals using MESC are H_2 (microbial electrolytic cell), biofuel (ethanol), volatile fatty acids (VFAs) (formate, acetate, and butyrate) (Li, Cai, et al., 2022), and other reduced C compounds (glycerol to propanediol) (Flynn et al., 2010).

Microbes are at the core of the MES, and their interaction with the electrodes governs the productivity and efficiency of the electrochemical process (Nguyen et al., 2024). In this chapter, various routes of electron exchange between microbes and the electrodes are briefly discussed. Microbial metabolic capacity to utilize the extracellular electrons for product synthesis has been

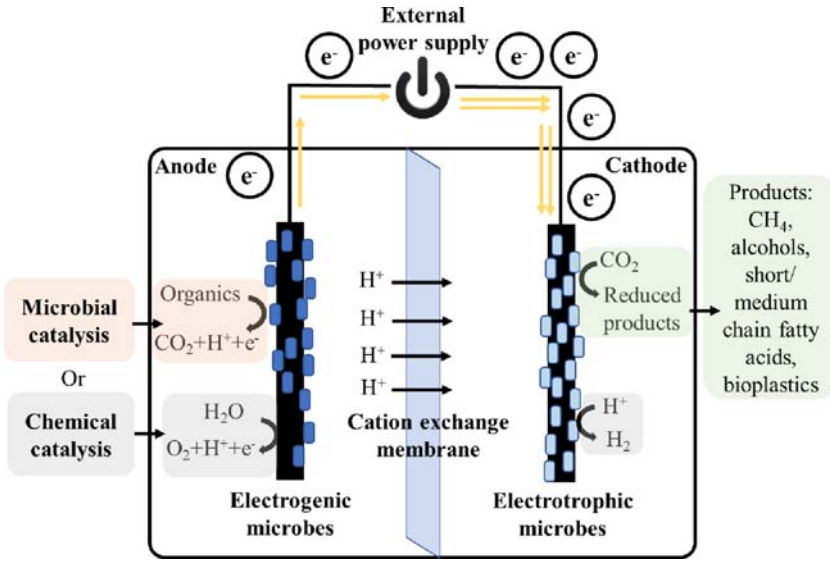

FIGURE 7.1 Representative microbial electrochemical synthesis cell.

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overviewed along with a brief discussion on widening the product spectrum using genetic engineering. A future perspective on challenges of scaling-up the technology and their possible solutions have also been presented.

2. Microbial catalyst for electrosynthesis

The electroactive microbial catalyst in the MES can be classified based upon its interaction with the electrode: electrogenic (electron donating) on anode and electrotrophic (electron accepting) on cathode (Logan, 2008). Electrochemical activity of yeast was first discovered by Potter in 1911 (Potter, 1911). Since then, several electroactive microbes have been identified that uses inorganic compounds such as Fe ions as terminal electron acceptor. In 2010, it was demonstrated that cathodic biofilms of *Sporomusa ovata* could produce reduced C compounds by electrochemical reduction of CO_2 and water (Nevin et al., 2010). These microbes were able to exchange electrons with electrodes in BES by forming biofilm over electrode surface. As shown in Fig. 7.2, biofilm consists of microbial cells embedded in cell-secreted exopolymeric matrix (EPS), and its formation is influenced by the electrode surface characteristics and external environment. Electron exchange can happen directly by producing electric pili and outer membrane cytochromes and indirectly by electron

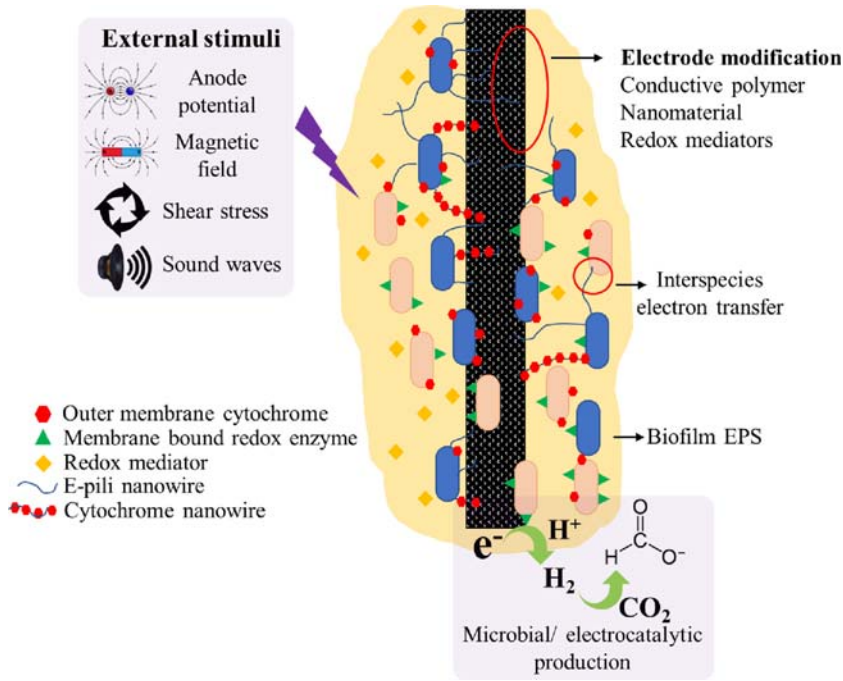

FIGURE 7.2 Microbe–electrode interaction.

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shuttles such as flavins, quinones, phenazines, humic substances, and EPS matrix; and interspecies electron transfer (Surti et al., 2022). Most of the theories on extracellular electron transfer have been studied on model electroactive microbes *Geobacter* and *Shewanella*. Several membrane-bound enzymes such as dehydrogenases and oxygenases have been implied for accepting electrons from the cathode. Moreover, electrochemically or microbially produced intermediates such as formate and H_2 can also mediate indirect electron transfer to cathodic microbial community (Karthikeyan et al., 2019).

Electrogenic microbes are expected to be metabolically versatile in utilizing the complex wastewater substrate at anode and oxidizing it to produce electrons. Microbial consortium is found to perform better in terms of removal of chemical oxygen demand (COD) from wastewater and better tolerance to environmental fluctuations as compared with pure cultures (Zhang et al., 2021). Successful biofilm formation over anode surface is a prerequisite for a well-performing MES. Electrode modification with conductive polymers and nanomaterials has been used for forming conductive channels between electrode surface and cell membrane and for increasing surface area to promote microbial adherence (Vassilev et al., 2022). Moreover, external stimuli such as positive anode potential, sound, magnetic field, and shear stress have also been shown to enhance biofilm formation (Bhagat et al., 2021, 2022). This helps reducing the start-up time of MES and hydraulic retention time (HRT) of wastewater in MES under continuous flow system.

Electrotrophic microbes must have an efficient electron capture system from cathode and channel the electrons into its metabolic circuit to produce desired product. Biocompatible cathode material, sufficient availability of substrate, and optimum reaction conditions such as pH, temperature, and ionic conductivity of catholyte influence the formation of cathodic biofilm and its productivity. Microbes that can fix inorganic C to short-chain fatty acids or alcohol with reduced by-products formation are desirable in MES. Diverse autotrophic and acetogenic microbes have been exploited at lab scale to produce value-added organics (Nevin et al., 2011). Syntrophic relationship is often established in mixed consortium at cathode in which electron uptake by one microbe provides an intermediate as feedstock for product formation by another microbe (Marshall et al., 2012). Enriched consortia forming cathodic biofilm of up to 10-μm thickness on three-dimensional carbon nanotube-based electrode have shown acetate production is comparable with conventional fermentation (Jourdin et al., 2015).

It has been generally accepted that the electroactive microbes and electrodes must be in close proximities for efficient electron transfers. Distance between anode and cathode must be minimal to avoid ohmic resistances. It is desirable to have a larger number of microbes for achieving higher production and current densities but not limiting the mass and charge transfers. The regulation of surface area to volume ratio of electrodes to electrolyte is the rate-determining factor of all MES (Roy et al., 2022).

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3. Wastewater substrate

MES is a sustainable and innovative tool that can be used to produce a variety of value-added products as resource recovery from wastewater has been a target of scientific community recently. The bioelectrosynthesis process utilizes various substrates such as waste gas, wastewater as well as solid waste for the production of value-added chemicals, and this technology is not dependant on the fossil fuels (Kong et al., 2020). In addition to acetate and glucose as substrate in the MES, the range has been widened to utilize other wastewaters as well as waste gases as shown in Fig. 7.3. With an external supply of CO_2 and electricity, MES can be used for direct reduction of CO_2 to produce short-chain organic acids. This process utilizes the greenhouse gas and recovers/recycles CO_2. Generally, at anode, oxidation of any organic matter takes place, and the produced electrons travel through the external circuit to reduce CO_2 at cathode, resulting in the production of short-chain organic acids. It has been observed that extensive research has been done on MES by using domestic wastewater as substrate and the degradation of same can result in the production of hydrogen gas, various acids, ethanol, and methane gas.

Chinese liquor brewery wastewater (CLBW) was treated at the anode compartment of H-shaped MES using CO_2 as C source at the cathode. The main objective here was to upgrade CLBW to biofuels such as medium-chain fatty acids. The continuous ethanol oxidation produced 4.37 g/L acetate and other products were 7.98 g/L caproate, 3.5 g/L propionate, 0.9 g/L isobutyrate, etc. (Zhao et al., 2023). Ma et al. utilized real winery wastewater to produce

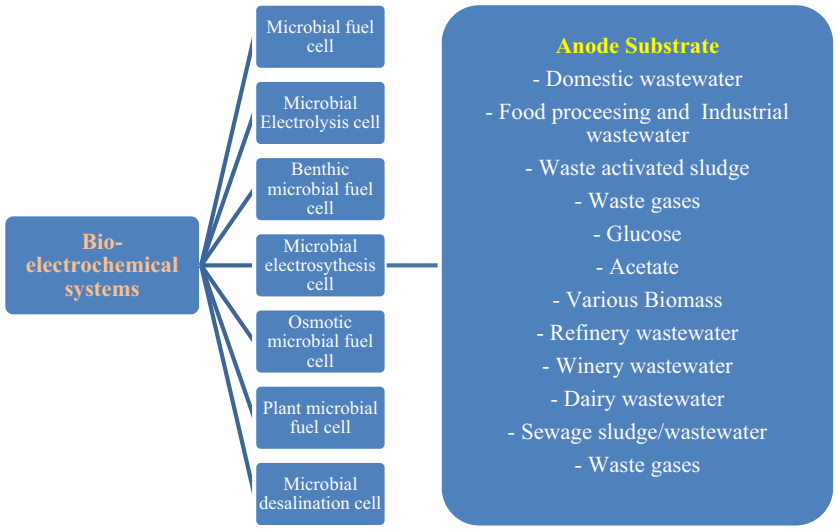

FIGURE 7.3 Various anode substrates used in bioelectrochemical systems.

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caproate at 2.37 g/L by applying −0.8 V of cathode potential (Ma et al., 2022). Anaerobic digestion sludge from a real wastewater treatment plant was oxidized at anode compartment of MES, and CO_2 was utilized as carbon source at cathode to produce 48 mM of acetate at applied potential of −1.0 V (Li, Kim, et al., 2022).

The CO_2 gas is used as a substrate at cathode in MES, which leads to reduction of greenhouse gas, and also, it should be noted that CO_2 is available in abundance and almost negligible cost. The reduction reaction of CO_2 as feedstock is possible only after solubilizing it by any abiotic or biotic method. In novel MES technology, dissolved CO_2 at cathode is converted into the various value-added products with the help of microbial degradation at anode. The external power output in MES can boost the CO_2 conversion producing various value-added chemicals at cathode as some of the reactions require higher energy output as per thermodynamics, which may not be fulfilled via electrons produced through microbial degradation at anode. The CO_2 gas is thermodynamically stable, and due to this, a large number of electrons may be needed to convert it into various value-added products (Christodoulou et al., 2017). In MES, acetate will be the main product at cathode if methanogenesis is inhibited.

4. Metabolic pathways for product synthesis

Microbially derived electrons collected at anode are used at abiotic or biotic cathode for electrosynthesis of product (Rabaey & Rozendal, 2010). Electrogenic microbes utilize anode as electron acceptor to drive their energy metabolism while oxidizing the organics in wastewater. It has been established that simpler molecule such as acetate produces higher current densities than complex molecules such as glucose or wastewater as oxidizable substrates due to simpler metabolism of acetate (Thygesen et al., 2009). Central metabolic pathways for amino acid, carbohydrate and lipid metabolism, xenobiotic degradation pathway, electron shuttle synthesis, and pathways for secondary metabolites synthesis are operational in anodic microbial communities depending upon the nature of substrate wastewater (Xie et al., 2021). Using abiotic cathode, electrochemical production of H_2, formate, acetate, and H_2O_2 can happen. Electrochemical catalysis is the driving mechanism for abiotic product synthesis at cathode.

Cathodic biofilm may uptake electrons directly from electrode or from electron mediators such as H_2, inorganic ions, CO, and formate (Claassens et al., 2019). The simplest products of MES with biotic cathode are acetate, butyrate, propionate, ethanol, and butanol. Electron uptake by microbes and subsequent reduction of cathodic substrates by microbial metabolic enzymes are the key to product synthesis at biotic cathode. A study by Kracke and Kromer identified 20 different products from electrically enhanced fermentation concluding that the electron transport rates at the electrodes and the metabolic potential for product formation are the major bottlenecks of MESC

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(Kracke & Krömer, 2014). The various products detected include succinic acid, lysine diaminopentane, isoprene, hydroxybenzoic acid, and aminobenzoic acid.

H_2 may be produced electrocatalytically or through biological hydrogenesis in MES. Almost 99% of electrons are captured by biologically produced H_2 and is assimilated into acetate by CO_2 reduction. Reductive acetyl coenzyme A–based Wood Ljungdahl pathway is central for acetic acid production in MES (as shown in Fig. 7.4). The product spectrum can be extended to alcohol and other short- to medium-chain fatty acids by solventogenesis and reverse β oxidation (Vassilev et al., 2018). Nanocatalysts have been reported for enhancing the productivity of various MES processes. Microbially synthesized Cu nanoparticles can modify the cathode surface to enhance H_2 production (Jourdin et al., 2016). A combination of Cu metal electrocatalyst and biocatalyst for respective production of formate and acetate from CO_2 has also been suggested to enhance the productivity of MES (Chatzipanagiotou et al., 2021).

Pure cultures of *Acetobacter woodii*, *Sporomusa ovata*, *Clostridium ljungdahlii*, *Clostridium kluyveri*, *Moorella thermoautotrophica*, *Shewanella* sp., *Geobacter* sp., *and Escherichia coli* have been used for production of VFA. There are certain advantages of using pure culture such as selectivity and higher coulombic efficiency, while mixed culture is more adaptable and versatile (Zhang et al., 2021). A genome-wide analysis of biocathode community of high product yielding MES (65% acetate and 34% H_2) was shown to be

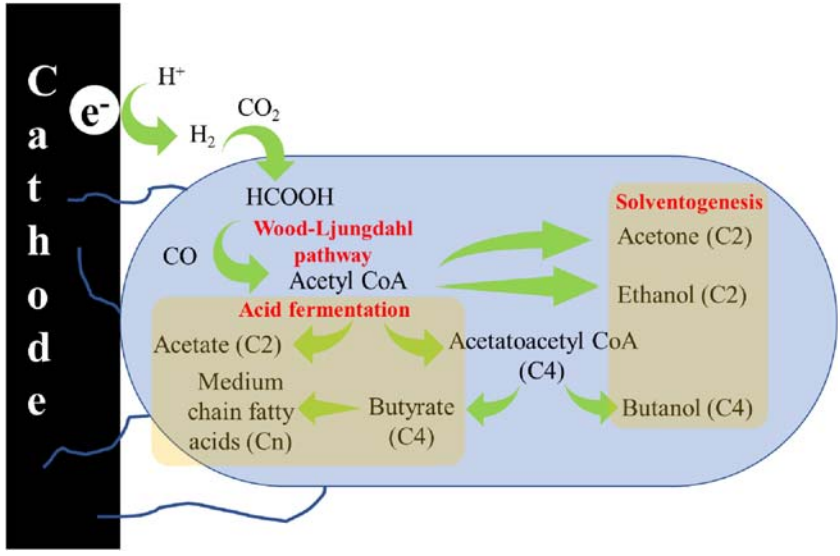

FIGURE 7.4 Metabolic pathways for product synthesis in electrotrophic microbes.

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dominated by *Acetobacterium*, *Sulfurospirillum*, and *Desulfovibrio* (Marshall et al., 2017). Metabolic profiling of this MES revealed *Desulfurovibrio* to provide hydrogenases and cytochromes for proton reduction to H_2, Acetobacterium to be the carbon fixer, and *Sulfurovibrio* is hypothesized to fix C by reductive tricarboxylic acid cycle. In a mixed consortium biocathode, the growth of methanogens can divert the electrons for methane production. Both acetogenic and methanogenic microbes thrive at the thermodynamic edge of life, leading to slower growth rate but high product yields (Claassens et al., 2019). A continuous supply of electrons to cathode is required for maintaining the acetogenic community in MES, while open-circuit conditions promote the growth of methanogens (Mateos et al., 2020). Since different pH optima are favorable for acetogenesis and chain elongation metabolism, a preenriched acetogenic biofilm promoted synthesis of C6 products by mixotrophic community (Wang et al., 2023).

5. Genetically enhanced microbial system

Genetic engineering has been employed to improvize the productivity of the MES by either of the two strategies: (1) incorporating novel metabolic pathway in electroactive microbes or (2) empowering existing microbial factories with electroactivity (Surti et al., 2021). The product spectrum of the MES has been increased by incorporating genes for biochemical conversion of substrate or chain elongation of acetate. Conventional anaerobic fermentation reactions are prone to unwanted by-products for balancing cellular redox status. The extra electrons can be diverted to anode to enhance the product formation and eliminate by-product formation (Förster et al., 2017). Genetically modified microbes have been employed for such electrofermentation process for enabling higher product yield. Table 7.1 shows few examples of genetically enhanced MES processes.

6. Production of value-added chemicals from wastewater

The MES technology combines the features of MFC where the degradation of organic matter at anode compartment produces electrons and MEC in which external power is required to drive the reduction reaction of CO_2 at cathode. This reaction is otherwise not possible without external output as CO_2 is highly stable thermodynamically. In MES, various value-added products are produced such as H_2, CH_4, formic acid, acetate, butyrate, ethanol, butanol, hydrogen peroxide, and metal recovery.

6.1 Formic acid

The production of formic acid at the cathode can be achieved by CO_2 reduction and microbial oxidation of organic matter at anode in an MES system. The

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TABLE 7.1 Genetically enhanced MES.

MES setup	Electron acceptor	Product	Anodic microbe	Cathodic microbe	Genetic modification	Yield	Reference
Single chamber	Fumarate	Succinate		*Escherichia coli*	Manipulation of flavin adenine dinucleotide (FAD) synthesis pathway	0.97 ± 0.02 mol/mol glucose	Wu, Wang, Zhang, et al. (2019)
Single chamber	Fumarate	Succinate		*Escherichia coli*	Electron transfer pathway from *Shewanella oneidensis*	1.10 mol/mol glucose	Wu, Wang, Liu, et al. (2019)
Dual chamber	CO_2	Poly hydroxy butyrate		*Ralstonia eutropha*	Expression of ribulose-bis-phospate carboxylase from *Synechococcus elongates*	485 ± 13 mg/L	Chen et al. (2018)
Single chamber	H_2 and CO_2 (exhaust gas of coal-fired power plant)	Lycopene		*Cupriavidus necator*	Expression of lycopene biosynthesis pathway	1.73 mg/L	Wu et al. (2022)
Single chamber	Anode	Para-hydroxy benzoic acid	*Pseudomonas putida*		Deletion of hydroxybenzoate monooxygenase and overexpression of chorismate pyruvate lyase	36 mg/L	Hintermayer et al. (2016)
Single chamber	Anode	Acetoin	*E. coli*		Expression of acetoin synthesis gene and outer membrane cytochromes from *S. oneidensis*	0.79 mol/mol glucose	Förster et al. (2017)

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formic acid can be produced by reaction: $CO_2 + 2H^+ + 2e^- = HCOOH$, which is a half cell reaction at cathode in MES. Yu et al. reported that electrosynthesis of organics from CO_2 can be achieved via *Moorella thermoautotrophica*. The immobilization of *M. thermoautotrophica* with carbon nanoparticles resulted in the formate production at 63.2 mmol/m^2day at −0.4 V and 55°C (Yu et al., 2017). It has been reported that the CO_2 can be reduced to formic acid at cathode of an MES system in the presence of enzyme formate dehydrogenase (Srikanth et al., 2014). In MES, 672.3 mg/L formate was produced by using Fe-C electrodes, and waste-activated sludge was used as a substrate in the study (Zhao et al., 2016).

6.2 Acetic acid

The acetic acid can be produced at biotic cathode in MES by two possible ways first in which CO_2 can be converted to acetic acid directly (Nevin et al., 2010) and second where it is produced with H_2 as a mediator (Zhen et al., 2015). It has been observed that acetogenic microbial organisms are capable to produce acetic acid (Mohanakrishna et al., 2016). The first time it was reported that 1.8 ± 0.2 g/L acetic acid can be produced from industrial CO_2 gas via MES technology, and it was also reported that mixed culture outperformed pure culture (Roy et al., 2021). In MES, for the first time, *Clostridium scatologenes* ATCC 25775^T was utilized as biocatalyst with resulting in 0.03 g/L production of acetic acid at −0.6 V potential and 0.44 g/L at −1.2 V potential (Liu et al., 2018).

6.3 Butyric acid

The butyric acid has many industrial applications and can be synthesized in MES in a sustainable way with little energy input. The butyric acid can be synthesized with electrons, protons, and acetic acid (Steinbusch et al., 2010). The hydrogen gas can drive the conversion of CO_2 into butyric acid at rate of 3.23 g/L and −0.8 V cathodic potential (Ganigué et al., 2015). The synthesis of butyric acid can be enhanced by acidogenesis, and the production was improved to 7.44 g/L day without any acetic acid (Choi et al., 2012). A triple-chamber MES system was designed for the production as well as separation of acetic acid produced from CO_2 at 81.35 ± 1.15 g/m^2 at −1.3 V potential (Das et al., 2021). The applied potentials of −0.6 and −1.2 V resulted in the production of butyric acid at rate of 0.01 g/L and 0.085 g/L when *Clostridium scatologenes* ATCC 25775^T was used as a biocatalyst for the first time in MES system (Liu et al., 2018). *Ralstonia eutropha*−assisted MES was able to reduce CO_2 to formate in a cathode chamber via formate hydrogenase (FDH)−catalyzed reduction reaction. The cathode potential of −0.6 V was applied to

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the system producing 485 ± 13 mg/L poly(3-hydroxybutyrate), which is three times higher than the control wild-type *R. eutropha* in the absence of FDH (Chen et al., 2018). The MES technology has been utilized to produce various other products as well as shown in Table 7.2.

7. Integration of microbial electrochemical systems with other advanced technologies

In recent years, the integration of existing wastewater treatment technologies with sustainable treatment solutions has been explored to overcome the limitations of conventional technology such as low efficiency, poor treatment, and carbon footprint. The integration of microbial electrochemical systems with other conventional or advanced technologies can be considered as a practical approach to enhance the performance. The CO_2 capture in MES can be combined with other technologies such as membrane separation, photobioreactors, anaerobic fermentation, enzyme-assisted MES, etc.

The MES technology was combined with membrane electrolysis (ME) by employing slurry electrode in a novel ME-MES system giving higher surface area to volume ratio. This integrated system was able to produce 13.4 g/L of acetate. The effect of powder activated carbon (AC) was also evaluated at cathode, and it was observed that the results were enhanced by almost 179% (Jiang, Chu, et al. 2020; Jiang, Liang, et al., 2020). The membrane contactors can be utilized for CO_2 capture and later on can be converted to methane via bioelectrochemical systems. In this study, real wastewater was used as CO_2 capture medium. The electromethanogenesis (EMG) with BES was operated at 0.7 V, and later on, four EMG-BES were stacked producing 4.6 L CH_4/m^2d (Rodríguez-Alegre et al., 2019).

The conversion of CO_2 into value-added products and its effectiveness in terms of energy source, raw material, and cost has gained a lot of attention from scientific community. Although low amount of external power input is required to reduce CO_2 at cathode in MES, the source of this additional energy input must be considered as it can add to the overall cost of operation during scale-up. It is very much advisable and practical if this energy input is from a renewable and sustainable source. The photovoltaic panels to harvest solar energy can be used to power MES for CO_2 reduction process. The MES can be also employed with photoelectrodes to enhance the harvesting of solar energy. The membrane liquid−liquid extraction can be used to extract VFAs produced from MES and anaerobic digestion (Kucek et al., 2016). The downstream processing of MES products is also a crucial step, and it may include purification, extraction, concentration, forward osmosis, nanofiltration, pervaporation, fractionation, etc. It should be considered that the overall operation cost of MES can be greatly reduced if such integrations are incorporated.

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TABLE 7.2 Production of various other value-added products in MES.

Reactor design	Mode of operation	Carbon source	Applied cathode potential (V)	Product	Production rate	References
H-shaped dual chamber	Batch	CO_2 and ethanol	−1	Caproate	2.41 g/L/d	Jiang, Chu, et al. (2020) and Jiang, Liang, et al. (2020)
Dual chamber	Continuous	CO_2	−0.85	Caproate n-butyrate	2 g/L/d 3.3 g/L/d	Jourdin et al. (2019)
Dual chamber	Batch	CO_2	−0.25	Methane	0.4 L/L/d	Xiao et al. (2020)
Redox flow battery design	Batch	Sodium bicarbonate	−1.08	Methane	12.5 L/L/d	Geppert et al. (2019)
Single chamber	Continuous	CO_2	−0.9	Methane	11.7 mM/d	Enzmann and Holtmann (2019)
H-shape dual chamber	Continuous	CO_2	−0.9	Acetate	0.436 g/L/d	Song et al. (2022)
H-shape dual chamber (two cathodes)	Batch	CO_2 Sodium bicarbonate	−0.7	Acetate	0.68 g/L/d	Bajracharya et al. (2022)
Double chamber	Fed batch	CO_2	−1	Acetate	7−10 g/L	Bajracharya et al. (2017)
H-shape dual chamber	Batch	CO_2	−0.9 to −1	Acetate	10 g/L	Bajracharya et al. (2017)
Dual chamber	Batch recirculation	CO_2	−1	Ethanol Butanol	8.46 g/m^2/d 3.12 g/m^2/d	Srikanth et al. (2014)
Single chamber	Batch	CO_2 and glucose	–	Succinate	1.1 mol/mol glucose	Wu, Wang, Liu, et al. (2019)

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8. Conclusion and future perspectives

MES system that can capture CO_2 gas and convert it into valuable products is an attractive alternative to conventional wastewater treatments, which can also help to reduce greenhouse gas emission. The MES platform can utilize renewable energy and produce various value-added products, and the overall cost can be reduced as some of the parts such as electrodes and separators are very costly. So, the power input source is a crucial factor for the scale-up of MES systems. On the other hand, the synthesis of low-cost separators and electrodes can be also considered. The better understanding of electron transfer at cathode is crucial for the improved production of VFA. The scale-up of these systems is not linear and can contribute to high ohmic losses. Although the idea of resource recovery and product synthesis using MES looks fascinating, high cost of assembly and operation, low yields, and poor efficiency of the process are challenging for scaling up of this technology (Prévoteau et al., 2020). There are very few studies available for scale-up systems and need further exploration for better working understanding of system. Wastewater as feedstock for microbial activity has highly variable characteristics and composition, limiting the consistent performance of MES.

The production rates of MES are not comparable to the commercially available other technologies, but certainly it can create an impact in terms of greenhouse gas capture and reduction. Integration of MES with existing synthetic technology may provide a suitable and practical solution until the bottlenecks of MES are strategically removed. To tackle the limitations of MES, it can be integrated with other conventional or advanced techniques, and it should be considered that the selection of downstream processing of MES is also a crucial element. The scale-up and optimization of MES-integrated systems can be dependent on collaborations between the scientist of different fields.

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Chapter 8

Advancements in the application of bioelectrochemical systems–based sensors

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Abstract

This chapter includes the research works on bioelectrochemical systems (BES) and their utility in powering different types of sensors such as water quality sensors, medical sensors, volatile fatty acid sensors, environmental sensors, plant growth sensors, etc. Recent advances and developments in sensor operations, electronics, and wireless data transmission and communication have enabled the widespread use of sensors in almost all technological fields, including engineering, medical sciences, chemistry, agriculture, etc. The use of BESs instead of chemical batteries is a safe environmental approach for sustainable development where waste management and powering of batteries can be achieved simultaneously. The BESs or more specifically microbial fuel cells (MFCs) or microbial carbon capture cells (MCCs) can effectively power water quality sensors and have the benefit of being a cost-effective and usage of clean energy source. Due to the high necessity for a newly emerging renewable energy supply with long-running life and high reliability, BES has a variety of possible applications in the modern technological scenario, and the performance of such systems is to be researched more in the future to enhance the efficacy. The recent trends in wastewater utilization and renewable energy production have paved a higher research option for the development of cutting-edge technologies such as BES acting as biosensors and power supply to different sensors. The suggestions for future research perspectives on BES are also highlighted in the chapter.

Keywords

Bioelectrochemical system; Microbial carbon capture cell; Microbial fuel cell; Sensors.

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1. Background

Bioelectrochemical systems (BESs) are electrochemical processes where biocatalysts or microorganisms participate in the oxidation or reduction reaction to consume electrons from the electrode surface or release electrons at the electrode surface (Jadhav et al., 2022, 2024). Different BESs are developed depending on the microbial reaction pathways, energy production or consumption characteristics, types of by-product harvesting, and types of oxygen sources. The microbial fuel cell (MFC) is a unique type of BESs, invented in the year 1911 (Picot et al., 2011, Potter, 2011). Gradually in the late 20th century and 21st century, other types of BESs are designed and investigated in laboratory and field scales such as microbial electrolysis cell (MEC), microbial electrosynthesis cell (MES), and microbial carbon capture cell (MCC) (Bhowmick et al., 2019, 2022). In MFC, the chemical energy stored in dissolved or suspended organics is anaerobically oxidized by biocatalysts or electrogenic microbes and harvest bioelectricity (Bhowmick et al., 2018), whereas in MEC and MES, external electrical potential is required to be imposed to synthesize biohydrogen, methane, or other useful by-products. In MCC, algae consume CO_2 and produce oxygen and maintain oxygen levels near the cathode surface (Neethu et al., 2018).

The MFC is a specific type of BES, which has several promising application potentials such as wastewater treatment, electricity generation, and biosensor-based applications (Bhowmick et al., 2020). The MFCs have the considerable potential of acting as an energy supply device for sensors, thereby providing the required electric current to power the sensors. The MFC itself can also act as a biosensor and detect refractory contaminants (Cui et al., 2019; Zhao et al., 2022) and heavy metals (Bagchi & Behera, 2020; Yu et al., 2017) and determine the biochemical oxygen demand (BOD) of the wastewater sample (Kim et al., 2003). Moreover, it is being observed that, in the medical field-specific, deoxyribonucleic acid or DNA strands can be detected by MFCs without an external analytical device (Ivars-Barceló et al., 2018). In addition to that, MFCs have proved its potential to supply power for several water quality, environmental, medical, and volatile fatty acid (VFA) sensors (Jiang et al., 2018). Nevertheless, MFCs have multiple advantages from a single system, making them cost-efficient and a renewable energy source.

2. Reason for selection of BES in powering sensors

BESs have a promising potential of powering sensors with high efficacy and low operational cost. BES specifically MFC can treat wastewater and simultaneously generate electricity for powering different kinds of sensors (Singh et al., 2023). Other than MFCs, MCC can also harvest electricity and be used as an energy-producing BES technology for sensors. The energy generated from the MFCs in the form of direct electricity is beneficial and sufficient to

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power different kinds of sensors such as water quality sensors (Khaled et al., 2016; Zhang et al., 2011), plant growth sensors (Nguyen et al., 2021; Veerubhotla et al., 2019), and so on. This is mainly because the sensors require very less energy for their operation. Several MFCs can be integrated or stacked to harvest more energy in substrate-lacking conditions for an uninterrupted stable power supply. In comparison with industrial wastewater, aquaculture wastewater has a low organic matter concentration. In such a situation, integrating several MFCs is advantageous.

The MFCs or other BESs also have the potential to act as a biosensor. Generally, sensors are powered by chemical batteries, which may be inconvenient in many situations since batteries must be recharged or replaced for a shorter period or have a limited lifetime. Waste batteries contain toxic chemicals and heavy metals, and improper disposal of these batteries is an environmental concern. Recent technological advancements in electronics, sensor operations, and wireless data transmission and communication have enabled the widespread use of sensors in almost all technologies, including engineering, medical sciences, chemistry, agriculture, etc. The use of MFCs instead of chemical batteries is a safe environmental approach for sustainable development where waste management and powering of batteries can be achieved simultaneously (Bahaa et al., 2023).

3. BES-powered sensors

Sensors are sort of those devices that sense or detect and respond to some kind of input from the physical environment and quantify the changes to measure the input. The measured input information is processed mainly using electronic systems or processors to provide the output value. Measuring pH, temperature, humidity, and heavy metal concentration are the most common applications of sensors in environmental engineering. Chemical sensors, wireless sensors, and miniatured telecommunication systems that have low power demand could be efficiently powered by BES-based sensors or MFCs. For a reliable sensor system, the essential factor is the stable performance of the sensor over the desired period. Water quality sensors, medical sensors, VFA sensors, plant growth sensors, etc. can be powered using BESs with lower operational costs and fewer environmental risks using a renewable energy source (Fig. 8.1).

3.1 Water quality sensors

Water quality monitoring is an important factor to provide clean and fresh water and understanding the contamination associated with it. Water quality depends on environmental, chemical, biological, and physical parameters such as pH, temperature, nutrient concentration, the concentration of organic and inorganic matter, the toxicity of heavy metals, etc. Water quality sensors are

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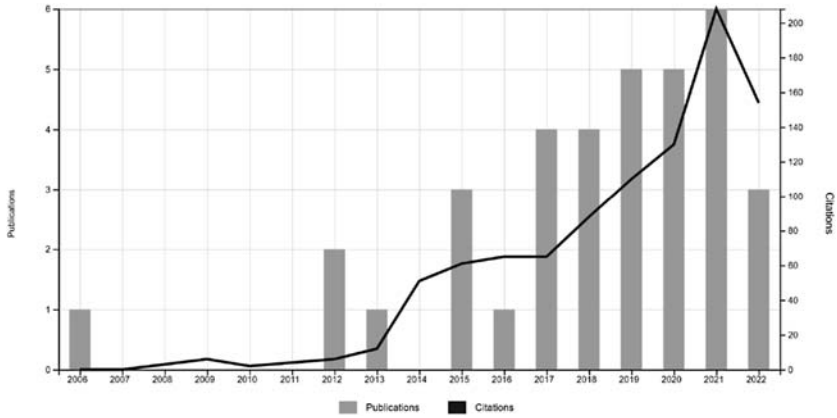

FIGURE 8.1 Number of scientific documents obtained from the web of science core collection between 2006 and 2022 using the descriptor—bioelectrochemical systems in powering sensors.

thus significantly commercialized due to their excessive requirements. The BESs or more specifically MFCs or MCCs can effectively power water quality sensors and have the advantage of being an economical and usage of clean energy source.

Different categories of water quality sensors can be powered by BES systems and can be efficiently powered using MFCs. The pH sensor (Brochu et al., 2020; Ivars-Barceló et al., 2018), dissolved oxygen or DO sensor (Schrader et al., 2013, 2016), conductivity sensor, salinity sensor (Schrader et al., 2013), turbidity sensor (Gong et al., 2011), organic loading rate or OLR sensor (Ivars-Barceló et al., 2018), and chemical oxygen demand or COD sensor (Shabani et al., 2021) are some of the few sensors that can be adequately powered by BES techniques, typically by MFCs. The conductivity sensor measures and monitors the electrical conductivity of water (total ionic concentration), whereas the salinity sensor checks the proper salinity level required in the sample as per norms. The turbidity sensor measures suspended solids by measuring the amount of light transmitted through water. The OLR sensor detects, monitors, and measures the organic loading rate of the sample. Future research may include powering the ORP (oxygen reduction potential) sensor, residual chlorine sensor, ammoniacal nitrogen sensor, and TOC (total organic carbon) sensor via BES systems. Typically, MFCs can act as a biosensor and help detect these parameters, indicating why there is no need for additional powering of these sensors.

An acoustic modem and marine oxygen and temperature sensor system have both been shown to benefit directly from benthic MFCs (BMFC) (Gong et al., 2011). Through the production of energy to operate the sensors and communication devices, the MFCs have shown their potential for remote ocean monitoring. A variety of environmental sensors may be powered by

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BMFCs, which have also demonstrated their feasibility and affordability as a long-term, continuous power source for submarine devices (Gong et al., 2011). The BMFCs power the seawater oxygen sensor, which measures the seawater's ambient DO level, the temperature sensor, and the acoustic modem, which is used to transmit information from the sensor. A sensor that measures air and water temperature and broadcasts the information to a distant receiver via a telemetry system can be powered and operated by MFCs (Shantaram et al., 2005). The MFC was combined with a greatly efficient, low-power electronic circuit, and a capacitor was utilized for the storage of energy that is produced by MFC to produce sufficient electrical energy to the telemetry system.

A sediment MFC (SMFC) has the potential to act as the power supply to a wireless temperature sensor, and the corresponding sediment MFC can be utilized as an effective renewable power producer (Donovan et al., 2008). Two SMFCs were able to effectively power a wireless temperature sensor by using Lake Michigan sediment and stated constant electricity production (Zhang et al., 2011). Similarly, two MFCs powered a temperature sensor in a continuous and autonomous operation mode for 2 days (Khaled et al., 2016). A power management system (PMS) with a commercial direct current (DC)/DC convertor and two capacitors was used to assist MFCs in powering the temperature sensor. A wireless sensor can be powered using a sediment MFC for a long time not requiring external control on the unit, which was demonstrated by several researchers (Khaled et al., 2016; Thomas et al., 2013). The sediment MFCs were used to power wireless sensor network (WSN) nodes and showed very stable performances with very less maintenance without any membrane or artificial catalysts. Also, BMFC with an attached PMS has the potential to power up two subsea temperature sensors (Liu et al., 2015).

An average power density of 44 W/m^2 of seabed area can be produced by BMFCs, which in fact can power marine sensors that measure ocean salinity, pH, water current velocity pressure, turbidity, relative humidity, air temperature, and water temperature (Gong et al., 2011). A water quality sensing unit device that is an energy-autonomous system employed a single MFC as its sensory input as well as the main power supply to measure and monitor COD (Shabani et al., 2021). The MFC also performed as a power source for the microcontroller that records MFC voltage and is capable of continuous operation and estimation of COD value. In an autonomous energy system, larger MFCs are recommended for energy generation as a lot of energy from biomatter is provided to the MFC at once. MFCs could be operated as the power supply for organic loading rate (OLR), pH, and temperature sensors (Ivars-Barceló et al., 2018). The organic loading rate is the rate of BOD per unit volume of sample, which is an indicator of the unit weight of biomass of microbes present in it, which is used to compute MFC's substrate conversion.

The pH sensors monitor the pH, i.e., the negative logarithm of the hydrogen ions concentration in the aqueous solution can also be powered using MFCs. An ultralow power pH sensor was able to utilize the electrical energy

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generated by MFC could power a signal processing and control unit and analyze signal processing chips to develop a green energy portable pH sensor (Brochu et al., 2020). Independent BMFC powering sensors have different applications in acoustic communication as well, and BMFCs have proved their efficacy in powering temperature, oxygen, salinity, and conductivity sensors (Schrader et al., 2013). It was observed that the BMFCs could power these oceanographic sensors, which can reliably measure DO, salinity, conductivity, and temperature throughout their operational life (Schrader et al., 2016).

3.2 VFA sensors

BES sensors have demonstrated their popularity as straightforward, affordable options for continuous monitoring of volatile fatty acids during the anaerobic digestion process (Jin et al., 2017). VFA sensors gauge the amount of volatile fatty acids produced during anaerobic digestion. The VFA concentrations measured by the biosensor and analyzed by gas chromatography were closely correlated. The results demonstrate that this biosensor with a novel design may be used to track VFA levels as Alzheimer's disease progresses (Moreira et al., 2017). A novel air cathode MFC having two chambers comprised of a single-chamber MFC and a sample chamber separated by AEM was built and tested to determine the technical potential of such a system as a biosensor for VFA sensing in the AD process (Sun et al., 2021). From the sample container to the anode compartment, VFA will migrate. There, electroactive bacteria will oxidize them and to produce energy, electrons are moved from the anode to the cathode that is exposed to the air. Single-chamber MFCs have been built as online shock sensors to detect the VFA concentration in anaerobic digesters, and their potential as efficient biosensors has been determined (Schievano et al., 2018). Using acclimatized mixed bacterial populations, MFC-based biosensors for monitoring specific volatile fatty acid concentrations were constructed, and a positive connection was estimated between VFA concentration, charge, and current produced (Kaur et al., 2013). This MFC-based biosensor had the potential to measure the individual acetate, propionate, and butyrate concentrations.

3.3 Medical sensors

Currently, the majority of medical sensors and internal medical devices rely heavily on lithium batteries due to their comparatively higher energy density and reliable and consistent performance. However, their lifespan is substantially shorter, and they must be constantly recharged or replaced. Thus, there is a great need for an emerging renewable energy source with a long lifespan and high dependability. To monitor and analyze the DNA immobilization and hybridization events, an analytical apparatus was created using an MFC system as a power generator (Asghary et al., 2016). Current research focuses on

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the implantation of MFC within the transverse colon of the large intestine to power implanted medical devices (IMDs). Researcher Han and their colleagues observed that after 2 months of operation, MFC produced steady power on an open-circuit voltage (OCV) of 552.2 mV, a peak power density of 73.3 mW/m^2, and an output voltage average of 308 mV with an external load of 500 Ω (Han et al., 2010). The proposed research describes IMDs that can be powered by MFCs installed in the human colon to exploit microorganisms and intestinal material for electricity generation. MFC has the capacity to generate 7−10 mW, which is sufficient for IMDs, and MFCs positioned in the large intestine can serve as a stable alternative power supply for IMDs.

Currently, research is being conducted on a wearable, biosensor system, which can be self-powered that is paired with a diaper to monitor diabetic patients' urine glucose (Zhang et al., 2011). The technology was powered by an enzyme biofuel cell (EBFC) that used the glucose in urine as fuel to generate energy. The EBFC was constructed in a diaper and connected to a PMS with a capacitor for energy storage. Recently, MFC-based DNA biosensors have been introduced as systems for DNA detection that can perform precise sequencing without an alternative power source. These systems use a dual-chambered MFC system to develop an analytical device for the characterization and continuous monitoring of DNA immobilization and hybridization events (Asghary et al., 2016). Any discrimination between complementary DNA sequences, such as one-base mismatched or noncomplementary sequences, was shown by the MFC's power output, which also revealed the hybridization of the DNA probe. Human serum was employed as a sample, and the results revealed a high degree of sensitivity, remarkable stability, and adequate repeatability.

The MFC energy supply system has proved its efficacy in powering a piezoresistive pressure sensor along with an ultrawideband transmitter (Tommasi et al., 2014). The piezo-resistive sensor is commonly employed in medical devices, such as blood pressure measurement equipment, for the measurement of mechanical stress. Enzymatic biofuel cells (EBCs) are a form of biofuel cells that oxidize their fuel using enzymes as a catalyst. Cell-free EBCs were utilized to power artificial hearts, which can be implanted, marking the first usage of MFCs in IMDs in the period of 1960 (Bullen et al., 2006; Yahiro et al., 1964). It has a variety of uses in self-powered biosensors and self-powered wearable sensors. In an attempt to power IMDs, EBCs that used oxygen as the oxidizer and glucose as the fuel was investigated in the 1970s (Wei & Liu, 2008), and numerous methodologies and modifications have been presented since then to improve performance and target-specific applications. Mano and colleagues stated in 2003 that they had developed a tiny biofuel cell that could operate while being placed inside a grape by generating a power of 2.4 W at 0.52 V, which is very much effective for tiny implant applications (Mano et al., 2003). Infection is not a significant problem since anaerobic bacteria are prevalent in the intestinal mucosa, whereas

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aerobic microorganisms are prevalent in the lumen that discharges through excretion. Han et al. (2010) have started an MFC-based IMD research of implanting in the large intestine, which seemed effective. With the existence of mitochondrial that operate as biocatalysts, certain research publications have identified probable IMD-MFCs. Strong biocatalyst activity and exceptional biocompatibility between conditions have contributed to the device's outstanding performance and reduced total cost. However, the potential of the technology under study was restricted by a lack of microbe selectivity.

When an analyte interacts biologically or chemically with its environment, electrochemical sensors analyze the electrochemical species that are absorbed and/or created. The working electrode acts as the transducer of the electrochemical reaction in the case of implant deterioration, with redox reactions taking place on the surface and structural variations producing surface modifications. Not surprisingly, the first autonomous enzymatic biosensors focused on glucose. In this scenario, glucose is oxidized at the anode by an oxidoreductase enzyme, while cytochrome *c* oxidase consumes oxygen at cathode. Other enzymes were also added to this design; however, it is believed that glucose serves as the fuel for the fuel cell. This approach has been applied to some other analytes as well, including fructose (Miyake et al., 2011; Baingane & Slaughter, 2017), acetylcholine (Moreira et al., 2017), ethanol (Ruff et al., 2017), oxygen (Falk et al., 2014), ascorbic acid (Zloczewska et al., 2014), and cholesterol (Grattieri & Minteer, 2018; Sekretaryova et al., 2014).

3.4 Environmental sensors

Advancements in smart agriculture techniques, Internet of things (IoTs), sensors, etc. have enhanced agriculture productivity and disease risk reduction. Smart agriculture is a revolutionary step in the agricultural sector that has helped automate irrigation systems and monitor the crop field, i.e., light, humidity, temperature, crop health, soil moisture, etc., with the help of sensors. The power supply of these sensors has a higher demand in this advanced smart farming revolution. The MFCs have the potential to power sensors with low power as well as low voltage characteristics of the distributed WSN.

The BESs are power generators that have applications in plant growth, disease detection, and risk reduction and can power all the plant growth sensors that require a very considerable amount of energy. Plant MFCs are also developed (PMFC), which can replace the use of batteries for sensors, WSNs, IoT, and machine communication systems. The PMFCs are clean, renewable energy sources that promise a potential power supply for sustainable low-power-required sensors. PMFCs can be installed in greenhouse monitoring as well as precision farming techniques.

Terrestrial MFCs generally operated outside waterbodies where cathodes are air-facing and anodes buried in moist soil. Soil acts as both a proton exchange membrane and electrolyte. This setup has been identified as a power

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generation system or smart agricultural applications and plant health monitoring applications. Terrestrial MFCs have been applied in precision agriculture and land monitoring to power up a WSN (Ancona et al., 2020). The results indicated that MFCs could harvest sufficient energy to power the pH sensor as well as soil humidity sensors and deliver the information to WSN, where the receiver processes the information. A soil moisture sensor that measures the current moisture content at the root zone is generally used for measuring soil water content. Soil MFC has been used for sensing soil water content in agricultural fields and has the potential for power generation for soil moisture sensors (Nguyen et al., 2021).

The wireless IoT temperature sensor module, which detects and senses temperatures and transmits data to a smartphone, was able to be driven by frugal paper-based MFCs by harvesting electricity that is then stored in a supercapacitor (Veerubhotla et al., 2019). The IoT sensor modules can measure several physicochemical parameters such as temperature, humidity, light intensity, etc. Humidity and temperature sensors were powered effectively using an individual MFC in a PMS and used for unmanned environmental monitoring (Zheng et al., 2015). The PMS was built based on a charge pump using the supercapacitor to collect and store energy. With the assistance of PMS, the external sensors or any load could be powered by an individual MFC. By utilizing graphite electrodes with reduced oxygen on the cathode, Tender and his colleagues oxidized reduced compounds in the sea bottom sediments close to Tuckerton and Raritan Bay, New Jersey (Lowy & Tender, 2008; Tender et al., 2002). Delong and Chandler have proved that microbial fuel cells can be operated in the sea or ocean to power sensors and recommended using the cathodic reaction to reduce oxygen and the anodic reaction to oxidize sulfide created by microbes (Shantaram et al., 2005).

Many researchers replicated the marine environment on a lab scale and demonstrated that electricity generated from MFC is highly suitable and adequate for oceanographic sensors and other marine instruments used for ocean conditions monitoring for a longer time period (Tender et al., 2002). The voltage gradient that results from sediment microbial activity at the water−sediment interface may be effectively used to produce electricity using a fuel cell made up of an anode implanted in sea sediment and cathode in the surrounding seawater. Such MFCs that are employed in water bodies have the potential to generate enough electricity for sensors with lower power requirements. Submersible ultrasonic sensors, specially designed for fisheries and wildlife research (a kind of remote sensor) used for underwater sensing, can be powered using an SMFC (Donovan et al., 2013). The SMFC was assisted with a PMS that had the potential to power and operate a submersible ultrasonic receiver (SUR), which is able to sense ultrasonic signals and record the motion of fishes along with various aquatic species attached to ultrasonic transmitters. The SMFC system proved to have the ability to power underwater SUR sensors for an extended period (6 weeks) of environmental monitoring without conventional batteries. This is

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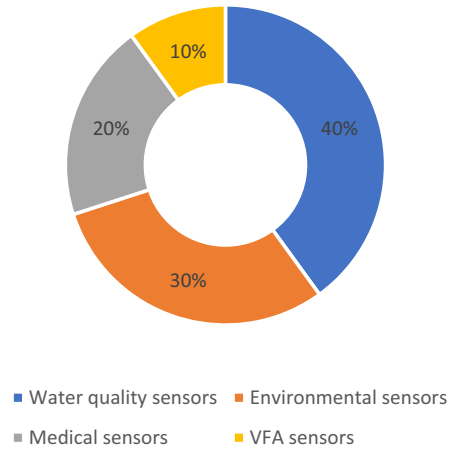

FIGURE 8.2 Approximate percent of research works done on sensor systems effectively powered by BES (web of science datawise).

how different types of sensors developed or investigated by different researchers from around the globe to be powered by BESs (Fig. 8.2).

4. MFC itself as the biosensor

The MFCs themselves can act as a biosensor and can analyze BOD, electrical conductivity, salinity, COD, etc. (Klevinskas et al., 2021). A biosensor is a system which uses certain biological processes to detect the presence, absence, or variation in chemical component concentrations using thermal, electrical, or optical signals (Abrevaya et al., 2015). This technique merits easy access for onsite, real-time, cost-effective monitoring, and high simplicity of ease. The MFC-based sensors act as water quality monitoring devices as well as water toxicity sensors. Low selectivity, risk of microbial contamination, mass transfer limitations, and low detection limits are some of the general limitations to consider while using MFC-based sensors. The biosensor can sense temperature, pH, redox potential, conductivity, BOD, and specific chemical concentration and store or transmit time-resolved data (Fig. 8.3).

The BOD is a significant water quality parameter where the usual BOD test is time-consuming, and the real-time monitoring and rapid feedback are tiresome in the conventional BOD analysis. The first BOD analysis using MFC-based biosensors was demonstrated in the late 90s (Zhou et al., 2018). Recently, MFCs have shown their advancements in investigating the BOD of a wastewater sample and giving onsite measurement data of the total organic matter content. As a result, MFC-based biosensors are extensively applicable for this type of water quality analysis.

A marine MFC biosensor was developed and found to be efficient for detecting assimilable organic carbon (AOC) in seawater (Quek et al., 2015).

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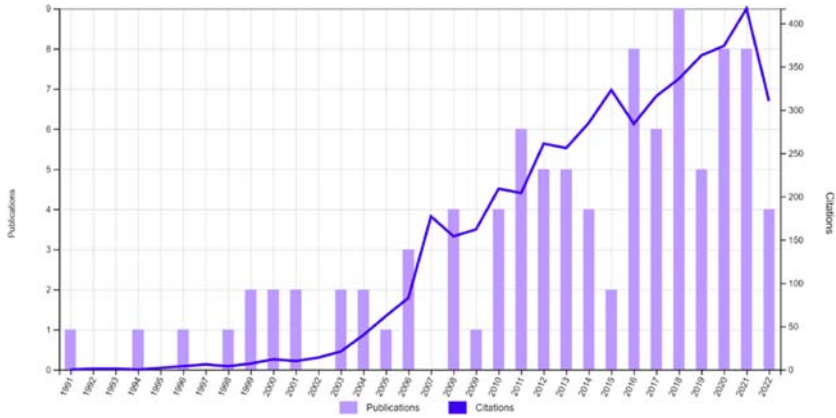

FIGURE 8.3 Number of scientific documents obtained from the web of science core collection between 1991 and 2022 using the descriptor—bioelectrochemical systems—based biosensors.

That biosensor has shown great potential to be a biofouling indicator for seawater reverse osmosis systems. The marine MFC has the potential to be effectively operated as a biosensor to sense, detect, and measure AOC, and the MFCs' generated electrical signals can be utilized to determine the concentration of acetate. An MFC-based biosensor can be effectively used especially for detecting BOD of wastewater, and this BOD sensor can be stably utilized for 5 years by not servicing (Kim et al., 2003). Carbon monoxide is toxic to most of the microorganisms except a few, such as *Clostridium* species that utilize CO as substrate. Generally, a typical BOD sensor that works on DO monitoring has limited stability due to the DO probe nature (anode metal gets easily oxidized). Thus, it is essential to clean the anode surface and change the electrolyte, which is problematic. Whereas the MFC-based BOD sensor was operated for 5 years without servicing under the condition that wastewater supply is not limited, an MFC-based biosensor for monitoring carbon monoxide (CO) has also been reported and found to be effective in its process (Zhou et al., 2018). They have demonstrated the feasibility of MFC for high CO concentration monitoring and reported the correlation between CO concentration and voltage. The anode's bacterial activity is often inhibited by CO, and a proportionate linear correlation between CO content and the voltage drop was shown to exist between 10% and 70%. Although certain *Clostridium* species may be able to use CO, majority of the microbes find it toxic. MFC-based biosensors were efficient for the purpose to detect BOD and specific pollutants toxicity such as formaldehyde, and cuprous ion (Cu^{2+}) employed mainly for environmental monitoring (Sun et al., 2015).

MFCs also showed their efficacy as a bioelectrochemical sensor for detecting and measuring the concentration of nitrite ions in water quality analysis (Klevinskas et al., 2021). The MFC-based biosensors had been

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researched to monitor a number of parameters, such as BOD, organic pollutants, heavy metals. VFAs, DO, toxicants, COD, antibiotics, and microbial activity (Klevinskas et al., 2021). The MFCs' current output is correlated with the metabolic activity of the electroactive biofilm that is present in the anode. Any atypical changes or impacts on metabolic pathways result in a change in the power produced. The continuous current variation might be connected to the specific disruption used when the feeding solution's operating characteristics, such as PH, conductivity, and temperature, are maintained constant. In MFCs, coupled oxidation on the anode and oxidant reduction on the cathode ensure the driving potential. This process is generally the fundamental working principle of the utilization of MFCs as electrochemical microbial biosensors.

Temperature and humidity sensors are also powered by MFCs. A PMS is a device that harvests energy using a charge pump and a supercapacitor (to store energy). When the PMS is switched on, the supercapacitor collects energy in short supplements throughout the charge phase and delivers it to a DC−DC boost circuit in the discharge phase. The cyclical operation of this PMS allows an individual MFC to feed an external load. Humidity and temperature sensor are powered concurrently by a voltage of around 5 V produced by the DC−DC boost circuit. The created circuit has achieved the objective of capturing the energy slowly building up from a single MFC and utilizing it to power the sensor and telemetry system (Zheng et al., 2015). A DC−DC boost circuit was used in a remote temperature and humidity sensor experiment to increase the voltage and power supply, thereby testing the system's functionality. The circuit has the ability to increase MFC adoption and offer a variety of applications in the unmanned environmental monitoring field.

MFCs act as self-powered biosensors since they have higher intrinsic sensitivity to physicochemical and biological parameters. Some applications include monitoring BOD, pH and temperature variations, toxic metal concentration, microbial activity, biofouling of electrodes, and biocorrosion of microbial biofilm (Cui et al., 2019; Ivars-Barceló et al., 2018). Compared with conventional biosensors, MFC-based biosensors provide higher sensitivity and stability. Different types of BES benefitted sensors and referred pieces of literature are shown in Table 8.1.

5. Future scopes

Although serious investigations on BES sensors are going on, considering the uncertainty of microbial culture and its response in different operating conditions, standardization of the operating parameters is necessary to achieve a reliable and repetitive sensor signal from the BES-based sensors (Table 8.2). There is a huge scope for exploring the sensing ability of different physical, chemical, or physicochemical parameters using BES sensors. Understanding the sensing ability of different pure culture microbial consortiums is also

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TABLE 8.1 Different types of BES benefitted sensors and literature included.

Sl no:	Sensor systems which can benefit from BES	Application of the sensor	Research included in BES-applied sensor systems
1	Temperature sensor	It monitors the system and/or surrounding temperature.	(Donovan et al., 2008, 2013; Gong et al., 2011; Ivars-Barceló et al., 2018; Khaled et al., 2016; Liu et al., 2015; Schrader et al., 2013, 2016; Shantaram et al., 2005; Veerubhotla et al., 2019; Zheng et al., 2015)
2	Humidity sensor	It senses the humidity of the surroundings.	(Ancona et al., 2020; Gong et al., 2011; Zheng et al., 2015)
3	pH sensor	It monitors the hydrogen ions concentration in the sample solution.	(Ancona et al., 2020; Brochu et al., 2020; Cui et al., 2019; Gong et al., 2011; Grattieri & Minteer, 2018; Ivars-Barceló et al., 2018; Sun et al., 2015; Zhao et al., 2022)
4	DO sensor	It monitors the dissolved oxygen level in the water.	(Cui et al., 2019; Gong et al., 2011; Grattieri & Minteer, 2018; Ivars-Barceló et al., 2018; Schrader et al., 2013, 2016; Sun et al., 2015; Zhao et al., 2022)
5	CO sensor	It monitors the carbon monoxide level.	(Zhou et al., 2018)
6	OLR sensor	It detects, monitors, and measures the organic loading rate of the sample.	(Ivars-Barceló et al., 2018)

Continued

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TABLE 8.1 Different types of BES benefitted sensors and literature included.—cont'd

Sl no:	Sensor systems which can benefit from BES	Application of the sensor	Research included in BES-applied sensor systems
7	Salinity sensor	It checks the proper salinity level required in the sample as per norms.	(Gong et al., 2011; Klevinskas et al., 2021; Schrader et al., 2013, 2016)
8	Conductivity ssensor	It measures the electrical conductivity of water (total ionic concentration).	(Klevinskas et al., 2021; Schrader et al., 2013, 2016)
9	COD sensor	It measures the chemical oxygen demand of the sample.	(Klevinskas et al., 2021; Shabani et al., 2021)
10	Turbidity sensor	It measures suspended solids by measuring the amount of light transmitted through water.	(Gong et al., 2011)
11	Soil moisture sensor	It measures current soil moisture at the root zone.	(Nguyen et al., 2021)
12	Piezo-resistive pressure sensor	The piezo-resistive sensor is known for its application in mechanical stress measurement and is widely used in medical devices such as blood pressure measurement equipment.	(Tommasi et al., 2014)
13	VFA sensor	It measures volatile fatty acids (VFAs) concentration produced during anaerobic digestion.	(Kaur et al., 2013; Schievano et al., 2018)
14	BOD sensor	It measures the biochemical oxygen demand of sample.	(Kim et al., 2003; Klevinskas et al., 2021)
15	AOC sensor	It detects and measures the assimilable organic carbon of the sample.	(Quek et al., 2015)
16	Submersible ultrasonic sensor	It is specially designed for fisheries and wildlife research (a kind of remote sensor), mainly used for underwater sensing	(Donovan et al., 2013)

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TABLE 8.2 Application of BES in sensor systems.

Sl no:	Application of BES in powering sensors	Application of BES based biosensors
1	Water quality sensors (pH, DO, conductivity, OLR, salinity, COD, CO)	Water quality based (BOD, DO, conductivity, COD, salinity, CO, heavy metals, toxicants)
2	Marine sensors (ocean salinity, oxygen, water temperature, pressure, air temperature, turbidity, water current velocity, pH, and relative humidity)	Marine based (salinity, AOC, conductivity, pH, temperature, DO)
3	Medical sensors ((IMD), piezo-resistive pressure sensor)	pH and temperature variation sensing
4	VFA sensor	VFA sensor
5	Plant growth sensors (pH, temperature, humidity, soil moisture, light intensity, electrical conductivity, soil humidity)	Detects biofouling of electrodes
6	Submersible electronic receiver (SUR)	Sense microbial activity, biocorrosion of microbial film

necessary, and thorough research is required in this regard. There is limited research on BES sensors other than MFCs, and the scope for other BES technologies needs proper investigation. An uninterrupted stable continuous power supply is necessary for BES-powered sensors, and considerable future scope for research is also available in this aspect.

6. Conclusion

A lot of commercial sensors and biosensors are generally powered using electrochemical batteries, typically batteries composed of lithium, and have very short life expectancy, or the batteries must be replaced or recharged frequently with possible environmental issues. This implies the importance of a sustainable renewable energy source that can generate enough power to charge these sensors or the energy source that itself can act as a biosensor. The

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BES comes to rescue the situation by acting as biosensors itself or to power the sensor devices. However, the unstable performance of BESs in variable temperature conditions is a concern, and adequate performance in extreme temperature conditions is a challenge in the operation it. Development of BES aims to achieve energy-efficient wastewater treatment, which should be durable, stable, sustainable, and cost-effective. Thus, BES, typically MFC, can act as a long-term alternative to conventional power generators or batteries to power the sensors with lower operational costs and environmental merits. These BESs have the multiple advantages of treating wastewater, acting as biosensors, and generating enough electricity to power the sensors.

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Chapter 9

Sustainability of microbial carbon capture cells for carbon sequestration and biomass generation

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Abstract

A microbial carbon capture cell (MCC) is an advanced version of microbial fuel cell, which guarantees the algal production alongside wastewater treatment and electricity generation. The technology is perceived as exceptional because of its added advantage of carbon sequestration and capability of recovering value added products from harvested microalgae. This chapter provides an overview of the principle, design guidelines, value added recoveries, and applications of MCC. Also, the main challenges and the future directions in scaling up MCC has been reviewed and highlighted in this chapter.

Keywords

Bioelectrochemistry; Electrogenesis; Microalgae; Microbial fuel cell.

1. Introduction

In the era where fossil fuel depletion and environmental degradation are directing the researchers to focus on energy transformation, solar energy is emerging as a promising profusion of clean energy source. The radiant light and heat liberated from the sun is utilized as solar energy by employing a range of technologies capable of transforming it to electrical energy, thermal energy, and so on. An innovative technology that exploits the photosynthetic efficiency of microorganisms and capable of effectively utilizing the dilute and intermittent nature of solar energy was the need of the hour (Sevda et al., 2019). Recently,

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microbial fuel cell (MFC), a technology capable of converting chemical energy present in wastewater to electrical energy with the assistance of electrogenic bacteria, gained much attention as an advanced value-added wastewater treatment technology (Jadhav, Chendake, et al., 2022; Jadhav, Park, et al., 2022). However, it has been reported that apart from the electrogens, certain other microorganisms including phototrophs can play crucial role in fostering efficiency of MFCs. The first attempt to achieve this was laid by Berk and Canfield in early 1960s by employing phototrophs in a bioelectrochemical system (BES) capable of simultaneous generation of electricity and carbon sequestration alongside wastewater treatment. A photoheterotroph, *Rhodospirillum rubrum*, was incorporated in the anodic chamber, and marine algae, *Oscillatoriaceae* sp., a photoautotroph at the cathodic side (Berk & Canfield, 1964).

The BESs are at the verge of commercialization, which is the result of immense innovations brought up by worldwide researchers on different elements of MFCs including the electrodes, oxygen reduction reaction (ORR) catalysts, proton exchange membranes (PEMs), microorganisms, mediators, design, etc. (Jadhav, Ghosh Ray, et al., 2017; Jadhav, Jain, et al., 2017; Jadhav et al., 2021). One of the notable advance was visible in the incorporation of phototrophs in BES, in both anodic as well as cathodic side. In addition to their role in enhancing the efficiency of fuel cell, phototrophs could tackle the problems associated with global warming, climate change, and greenhouse gas effect owing to their outstanding capability to sequester carbon (Bahaa et al., 2023). Based on the application of phototrophs, phototroph-based BESs are categorized as biophotovoltaic cells (BPVs), photosynthetic microbial fuel cell (PMFC), and microbial carbon capture cell (MCC). The BESs that employ living organisms that possess ability to perform photosynthesis including algae, plants, and certain bacteria including cyanobacteria are grouped as PMFCs, whereas BPVs are associated with phototrophs capable of generating extracellular current and hence are employed in the anodic chamber of BES (Wey et al., 2019). The MCC, as the name suggests, accomplishes the microalgae -assisted carbon sequestration along with wastewater treatment and electricity generation (Neethu, Tholia, et al., 2020).

Generation of energy from sources with reduced carbon emission is the most sustainable way to tackle issues associated with carbon emission including global warming and climate change (Quraishi et al., 2021; Yadav et al., 2021). Diverting the carbon dioxide produced in the anodic chamber, during the anaerobic treatment of wastewater, to the cathodic chamber employing microalgae makes the MCC a carbon neutral system capable of generating energy from wastewater (Vinayak et al., 2023). The ability of microalgae to transport and fix the bicarbonate into cells makes them the most valuable biological structure capable of capturing carbon alongside generation of huge feedstock for biodiesel production. Hence, incorporating microalgae into an MFC adds immense value to the technology in terms of carbon capture capability and as an aid to biodiesel production. This chapter on MCC is

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structured to provide an overview of the technology focusing on the mechanism involved in treatment of wastewater, carbon capture, electricity generation, etc. in an MCC. The chapter also provides current state of knowledge on various progresses in research related to MCC along with the factors affecting its performance. Since the choice of the technology depends on the end use, a section has been included about the application of MCCs and the scope of resource recovery. Finally, to provide a way forward to the researchers, the current challenges associated with the commercialization along with future direction are briefed toward the end of the chapter.

2. Technology overview

2.1 Electrogenesis

Electrogenesis is the process of generation of electrons by electrogenic bacteria, which are electrochemically active bacterial species with the ability to transfer electrons exogenously outside the cell (Kumar et al., 2015). These organisms are not taxonomically or physiologically classified or categorized; however, these possess extraordinary ability to transfer the generated electrons to external solid surface or liquid solution (Pandit et al., 2023). The transfer can take place either directly through conductive cytochromes/pili or via mediators (Table 9.1). The external solid surface acts as terminal electron

TABLE 9.1 Electrogenic microorganisms and their mode of electron transport.

Electrogenic microorganism	Mode of electron transfer	References
Pichia fermentans	Under microaerophilic condition capable of producing high power density conditions with methylene blue as mediator	Pal and Sharma (2019)
Arxula adeninivorans	Reported as mediatorless electron transfer	Haslett et al. (2011)
Shewanella oneidensis	Direct electron transfer Nanowires	Luo et al. (2023)
Geobacter sulfurreducens	Direct electron transfer	Li et al. (2022)
Clostridium butyricum	Electrochemically active with lower efficiency	Park et al. (2001)
Desulfovibrio desulfuricans	Presence of electron transfer proteins detected	Park et al. (1997)

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acceptor, which are majorly electrodes when applied in MCC. *Rhodoferax ferrireducens* and *Klebsiella* sp. *IR21* have the ability to directly transfer electrons to surface (Chaudhuri & Lovley, 2003). A maximum power density of 8.9 mW/m^2 was attained through direct transfer mechanism employing iron reducing bacteria (Lee et al., 2016). *Geobacter sulfurreducens* was reported to transfer electron via pili (Reguera et al., 2005). Mediators can either be self-secreted by bacteria as in *Shewanella* (Marsili et al., 2008) or could be artificial mediators such as methylene blue and neutral red (Pal & Sharma, 2019).

2.2 Carbon capture

At a moderate pH of around 6.5−10, the most prevailing form of CO_2 in aqueous body is bicarbonate, which are captured into the algal cells by transporters present in plasma membrane (Daneshvar et al., 2022). The bicarbonates are converted into CO_2 in the chloroplast and are fixed by rubisco producing three-carbon organic acid, which are reduced to sugar (Jadhav et al., 2024). Starch and lipid portion of the algal biomass are produced by utilizing these sugar molecules as substrate after CO_2 fixation through Calvin cycle (Dronsella et al., 2022). Production of a gram of algal biomass is associated with fixation of around 2 g CO_2 (Herzog et al., 2004). This property of microalgae opens scope for sequestration of carbon from a variety of sources including industries, fossil fuel power plants, anaerobic digestion systems, and so on (Fig. 9.1). A very interesting finding reported better algal biomass productivity through direct injection of flue gas into pond than obtained from

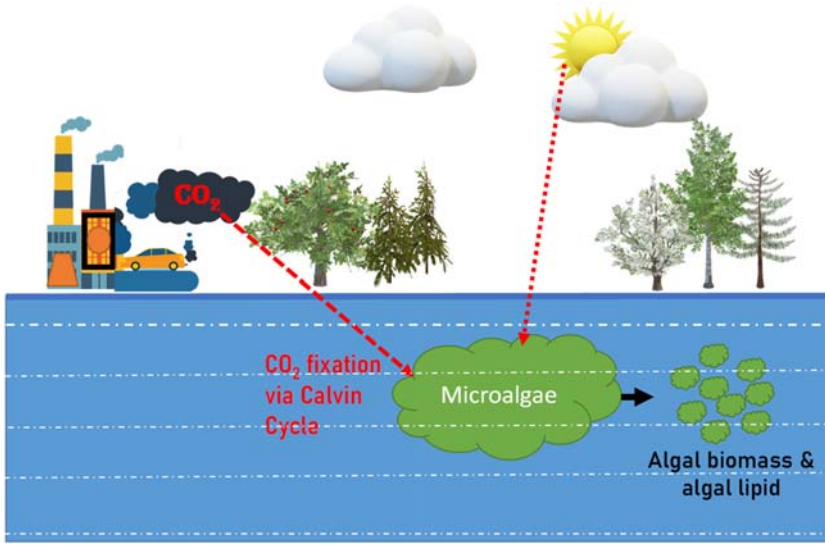

FIGURE 9.1 Carbon flow and fixation by microalgae in pond system.

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injection of equivalent amount of pure carbon dioxide, wherein the presence of nitrous and sulfur oxides in flue gas supplemented the algal biomass with nutrients for efficient nourishment by facilitating simultaneous flue gas bioremediation (Douskova et al., 2009). However, the carbon capture efficiency, which also depends on the algal physiology, pH, temperature, light, etc., can go as high as 99% provided optimum conditions are facilitated.

2.3 Microbial fuel cell

As the name suggests, an MFC is a biologically mediated fuel cell that converts unexplored chemical energy stored in wastewater to electrical energy. The organic matter present in the wastewater is biodegraded by exoelectrogenic microorganisms (Section 2.1), which results in production of electrons. The explicit role of electrogenic bacteria in the whole energy transformation process constrains the process to be mostly anaerobic (Jadhav & Chendake, 2019). Thus, the electrons produced in the anaerobic anodic chamber are captured by the anode and transferred toward the electron acceptor at the cathodic end via an external circuit. At the cathodic end, the electron combines with a terminal electron acceptor to get reduced (Logan & Regan, 2006). Oxygen has gained greater significance as electron acceptor in MFCs owing to the fact that on reduction the end product turns out to be harmless water. The anaerobes in MFC are capable of utilizing variety of substrate ranging from low COD municipal wastewater to organic matter—rich distillery wastewater (Elhenawy et al., 2022). Hence, application of MFC in treating wastewater is undoubtful; however, the current generation efficiency is the limiting part of the technology, which demands additional attention and immense research. While coupling wastewater treatment with electricity generation, several design and operational parameters come into picture. For instance, the electrodes, the proton exchange membrane (PEM), current collectors, electron acceptors, and so on bring about enormous challenges on the way to attain maximum power outcome (Neethu, Tholia, et al., 2020). The fact that the technology is at the verge of commercialization indirectly implies that significant research has been carried out to make MFC a sustainable competitor to the existing commercially available wastewater treatment technologies (Jadhav, Ghosh Ray, et al., 2017; Jadhav, Jain, et al., 2017).

2.4 Microbial carbon capture cell

An overview about electrogenic microorganism, microalgal carbon capture mechanism, and MFC technology is furnished in the aforementioned sections. An MCC is a modification of MFC with electrogenic bacteria in the anodic chamber and microalgae in the cathodic chamber (Jadhav, Neethu, & Ghangrekar, 2019). The mechanisms of operation of MCC and MFC are similar with the difference that in an MCC the oxygen, which is the terminal electron acceptor at cathodic side, is supplied by the microalgae via the process of photosynthesis (Fig. 9.2). As

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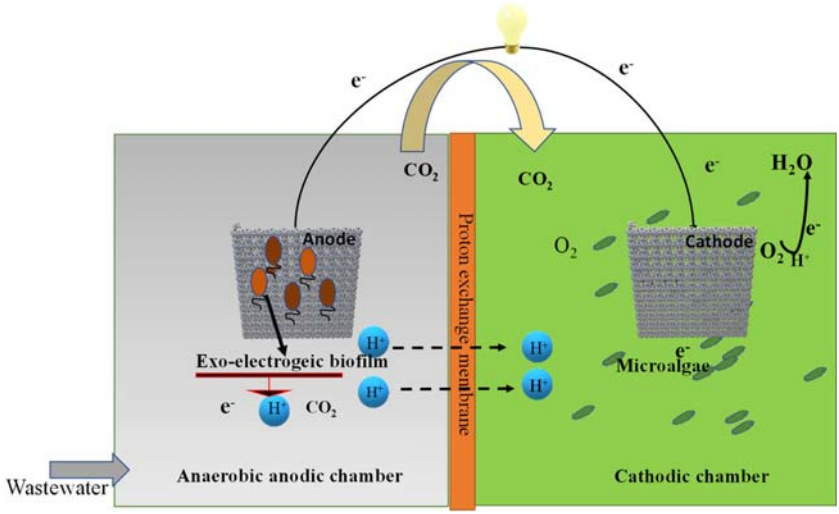

FIGURE 9.2 Schematic diagram of microbial carbon capture cell.

the name suggests, the microalgae in the cathodic side assist in capturing the anodic off gases, and interestingly, this property can be utilized in capturing the industrial and vehicular carbon emission. In addition to those mentioned for MFC, the factors affecting the performance of MCC include the microalgal physiology, photosynthetic efficiency, light duration/intensity, catholyte pH, carbon availability, and their mutual effects (Neethu, Tholia, et al., 2020).

3. Design and fabrication guidance

3.1 Proton exchange membrane

The membranes capable of transferring protons across them are collectively termed as PEMs; however, in an MFC, a PEM plays multiple roles in addition to its role as proton exchangers. A PEM acts as a barrier to passage of oxygen from cathodic chamber to anaerobic anodic chamber and also as an insulator to movement of electron through the membrane. Under certain circumstances, especially while employing ceramic separators, the PEM by itself acts as an anodic chamber. Application of different PEMs in MFCs and other BESs has been the focus of investigators over the past decade (Table 9.2). The Nafion membrane, with polytetrafluorethylene (PTFE) backbone and an end sulfonic acid unit, was once the most used PEM in BES researches. However, its associated cost along with flaws in properties including transmembrane transfer of oxygen and substrates, durability, etc. led researchers to think about low-cost and efficient alternative for Nafion membrane. Bringing about modification in Nafion membrane to overcome its defects was one way to achieve this. Membrane

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TABLE 9.2 Overview of proton exchange membrane materials used in MFC.

PEM material	Proton conductivity	Power density	References
Biochar–based PEM	0.07 Scm^{-1}	41.08 mW/m^2	Chakraborty et al. (2020)
Sulfonated oxy-polybenzimidazole	0.0783 S/cm	87.8 mW/m^2	Singha et al. (2016)
Sulfonated poly(ether ketone)/poly(ether sulfone) composite	6.93×10^{-5} S/cm	170 mW/m^2	Lim et al. (2012)
Ammonium-based supported ionic liquid membrane		103.9 mW/m^3	Hernández-Fernández et al. (2015)
Nafion	6.0×10^{-5} cm/s	1.9 W/m^3	Neethu et al. (2019a)
Ultrex		102.2 mW/m^3	Hernández-Fernández et al. (2015)
Activated carbon-clay based	9×10^{-5} cm/s	3.7 W/m^3	Neethu et al. (2019a)
PVA-H	0.13 $mol/cm^2.min^{-1}$		Liu and Lee (2021)
PVA/CCB-H Conductive carbon black	2.81 $mol/cm^2.min^{-1}$	171 mW/m^{-3}	Liu and Lee (2021)

pretreatment ranged from simple boiling to acid-based treatment owing to the fact that temperature and pH are the main parameters influencing the water absorption capacity and cation exchange capacity of a PEM, respectively (Jiang et al., 2016; Kuwertz et al., 2016). Microstructure modification of Nafion to facilitate proper channeling of protons by managing the pore connectivity has proved to improve the efficiency of the PEM (Safronova et al., 2022). Nafion-composite membranes, including sulfonated graphene oxide/Nafion composite, polydopamine/Nafion composite, graphene oxide/Nafion composite, TiO_2/Nafion composite, and so on, have added to the efficiency of PEMs (Cui et al., 2022; Li et al., 2023; Liu et al., 2022; Mayadevi et al., 2022).

The ceramic-based PEMs, which were first reported by Behera et al., were a major breakthrough in the field of MFC research (Behera, Jana, & Ghangrekar, 2010). Later constructive research was carried out by the same group on ceramic-based MFCs, which included thickness optimization, modifications, pH influence,

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cost analysis, etc. (Behera, Jana, More, et al., 2010; Behera & Ghangrekar, 2011; Raychaudhuri & Behera, 2020; Satyam B et al., 2011). Researchers globally laid their attention toward the ceramic PEMs and their modifications. Addition of cation exchangers including montmorillonite and kaolinite drastically improved the performance of PEM (Ublekov et al., 2014). Similarly, the incorporation of activated carbon, a low-cost filler, into ceramic-based PEM was another notable innovation in this field (Neethu et al., 2019b). Likewise, incorporating inorganic additives in hybrid polymer matrix enhances the physicochemical, thermal, and mechanical stabilities. Addition of 7.5 wt.% silica to SPEEK/PVdF-HFP was able to enhance the proton conductivity of PEM to 8.0×10^{-2} S/cm and delivered a power density of 1.5 mW/m^2 (Nayak et al., 2023). Also, phosphoric acid−doped SPEEK membranes were able to achieve power density double than that obtained by using Nafion membrane and showcased extremely high proton conductivity (Wang et al., 2023; Wu et al., 2023). Since the scaling up of MFC is more effective when MFCs with smaller volumes are stacked up, efficiency plays a major role than strength. As the time has arrived to move MFCs from lab scale to field scale, researchers should stay focused on development of low-cost efficient PEMs.

3.2 Electrode materials

Movement of electron within the cell is the major root of electricity generation in a BES, which is facilitated by a set of electrodes and connectors. Hence, electrodes play a significant role as performance influencing factor and cost determining element in BES. Electrodes can be either bioelectrodes, which are carrier of microorganism or can be chemical based. Unlike MFC, an MCC demands biocompatible material as electrode material. Certain other relevant perquisite of an efficient electrode material used in BES includes excellent conductivity, inertness, chemical stability, low cost, high surface roughness and area, etc. Certain material comes with these inbuilt properties; however, most of the cases demand surface modification to deliver better performance. For instance, catalyst is applied on a cathode-based material to improve the electron transfer and ORR kinetics. Similarly, bead-based electrode modification improved the surface area and imparted better bacterial adhesion in anode (Neethu, Bhowmick, et al., 2020). The good conductivity and inertness make the carbon material the largely used electrode material in MCC. Carbon electrodes can take plane structure as in carbon plate, paper, cloth, sheets, or packed structure in the form of granules applied as filling material or as carbon brush or felt. As far as the metals and metal oxides are concerned, non-corrosivity and biocompatibility are the major required characteristics as an electrode material apart from conductivity. Under this category, stainless steel and titanium proved to satisfy some of the requirements for good electrode material. However, the smooth surface texture of stainless steel reduces the bacterial attachment on the surface (Neethu, Bhowmick, et al., 2020).

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3.3 Light

In microalgae, being one of the core elements of algal-based fuel cell, light is a predominant efficiency-determining parameter. Providing sufficient light indirectly implies a light from a reliable source delivered at optimum intensity and wavelength for required duration. However, the complexity is much more when it is stated that this optimum condition differs from strain to strain and is dependent on several other factors including temperature. Hence, studies related to optimization of growth condition of each species through experimentation and modeling are significant. At a light intensity of 460 mmol/m^2 s, *Chlorella* zofingiensis exhibited a growth rate of 2.304/d; surprisingly, *Chlorococcum littorale* had a similar growth rate at a light intensity of 170 mmol/m^2 s (Imaizumi et al., 2016; Ota et al., 2015). Hence, it is evident that the optimum growth point of light is different for each species. As mentioned earlier, light intensity is dependent on temperature, as observed in case of *Chlorella miniate*. At a light intensity of 188 mmol/m^2 s, *C. miniate* exhibited a growth rate of 0.303/d and 0.376/d at temperature 14°C and 24°C, respectively (Sözmen et al., 2022). Culturing microalgae in an open pond brings out several disadvantages compared with a well-designed photobioreactor. One being the reduced intensity of light reaching the algae below the surface of open pond due to algal self-shading and more importantly is the growth inhibition due to unfiltered solar radiation reaching the pond (Holzinger & Lütz, 2006).

Usage of appropriate wavelength of visible radiation augments the algal growth; however, the desirable wavelength varies from species to species. Light wavelength in the range 420−470 nm (blue) and 650−680 nm (red) are considered to be highly beneficial to major proportions of microalgae (Gerdan Koc et al., 2023). Another recent advance observed in open pond cultivation is introduction of light filters capable of preventing incidence of unsuitable light radiations onto the microalgae. Wavelength filter was achieved with the aid of nanomaterial-based filter, wherein a 13%−34% improvement in algal yield was observed (Michael et al., 2015). Spectral conversion was achieved by specially fabricated luminescent acrylic filters, which absorbed specific light wavelength and reemitted it at a longer wavelength favorable to algal growth (Mohsenpour et al., 2013). One of the major challenges in scaling up algal-based MFC will be cost-effective delivery of light at its desirable intensity and wavelength. Even though artificially designed lighting system is opted considering the requirements, manipulated solar light either by filter or any other means will be the most advised one for large-scale system.

3.4 Terminal electron acceptor

The high oxidation potential and the capability of yielding clean end product on reduction makes oxygen the most commonly used terminal electron

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acceptor (TEA) for an MFC (Neethu et al., 2019b). Hence, oxygen-yielding capacity of microalgae is best utilized in an MCC, which uses the photosynthetic oxygen as TEA. Research in the field of TEA for MCC focuses majorly on two aspects, namely, enhancement of oxygen production by microalgae and exploration of algal friendly TEA. Apart from the oxygen production capacity of algae, the dissolved oxygen in water is dependent on factors including temperature, salinity, and presence of other foreign material. In case of microalgal oxygen production, pH and light quality and quantity are key parameters to be considered (Xue et al., 2011). In addition, inducing physical stress on algal cells has produced remarkable results. Microwave irradiation has increased chlorophyll-a, carotenoid, and protein contents of microalgae (Sivaramakrishnan et al., 2020). However, the irradiation effects of each species differently and hence optimization of radiation are significant (He et al., 2022). Low-cost ecofriendly physical stress induced by magnetic treatment was reported to improve the oxygen production with simultaneous enhancement in lipid content and algal growth rate (Tu et al., 2015).

Microalgae have a profound competence to confiscate nitrogen compounds including ammonia, nitrate, and nitrite from wastewater (Neethu & Ghangrekar, 2017). Biological denitrification in the cathodic chamber of MFC was first reported early in 2007, which proved the capability of nitrogen compounds to act as electron acceptor. A loop configuration wherein the effluent from anode is fed to cathode for denitrification by electron-served dual purpose of wastewater treatment and electricity generation (Virdis et al., 2008). Nitrate reduction at the cathode has alongside proven to yield a power density up to 7.2 mW/m^2 by generating ammonia as reductio product (Fang et al., 2011). However, a drop in voltage is obvious if nitrated get oxidized by electrochemical/biological process in the presence of oxygen (Puig et al., 2011).

4. Photosynthetic microalgae used in BES

Microalgae can be associated with BES system either as substrate in anodic chamber or as oxygen supplier in the cathodic chamber. However, the latter serves the purpose of carbon capture if designed and operated accordingly. Even though it is well known that green plants capture carbon dioxide, most of them fails to compete with microalgae in terms of photosynthetic efficiency, carbon capture efficiency, reproduction rate, and areal requirement. In addition to the aforesaid benefits, the value-added products generated from microalgae are much vast and substantial. Hence, incorporation of microalgae in MFC opens scope to expand the benefits of BES. Microalgal species are mostly cultivated in controlled environment that imparts required and controlled growth conditions. Incorporating microalgae in complex system such as BES brings out a number of challenges, which is very well addressed by researchers across the world.

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Photosynthetic efficiency, oxygen production capacity, ease of growth, resistance to adverse environment, nutrient removal efficiency, and lipid content are some of the characteristics to be investigated upon before incorporating a microalga into BES. For instance, the ease of availability and wastewater remediation capacity have assisted *Chlorella* sp. to impart remarkable contribution in MCC applications (Xiao et al., 2014). Also, a better removal of phosphorous and COD from the wastewater was attained by *Synechococcus* sp. as biocatalyst in MCC (Mohamed et al., 2020). *Chlorella sorokiniana* at an inoculum size of 20%v/v and light intensity of 140 μmol/m^2 fed into cathodic chamber of MFC effectively captured the anodic off gas as well as externally supplied CO_2, thereby yielding a maximum power density of 2.32 W/m^3 in dual-chambered MFC (Varanasi et al., 2020). Nutrients recapture and upcycling by several microalgal species have made them a promising candidate as biocatalyst in MCC (Table 9.3).

Coculturing of microalgae and bacteria in the anodic chamber of MFC also opens up wide scope for carbon capture using BES. Substrate exchange and exchange of signaling molecules during the algal bacterial symbiosis has substantially improvised activity of both the microbes (Sharma et al., 2022). The process involves supply of oxygen and organic carbon to bacteria and capture of carbon dioxide by microalgae (Ramanan et al., 2016). In an investigation, a ∼11% and ∼110% growth was observed for algae and bacteria through mutualistic interaction, which uproots the scope to enhance the efficiency of both electrogens and microalgae (Kim et al., 2014).

TABLE 9.3 Microalgal species employed as biocatalyst in MCC.

Microalgal species	References
Scenedesmus abundans	Nayak et al. (2019)
Desmodesmus subspicatus	Ribeiro et al. (2022)
Scenedesmus obliquus	Kakarla et al. (2014)
Chlorella sorokiniana	Gupta (2005) and Neethu et al. (2018)
Scenedesmus quadricauda	Yang, Pei, et al. (2018)
Nannochloropsis sp.	Shi et al. (2021)
Chlorococcum sp.	Mohamed et al. (2020)
Chlorella vulgaris	Pan et al. (2021)
Coelastrella sp.	Raja et al. (2022)
Oscillatoria agardhii	Mahmoud et al. (2019)
Golenkinia sp.	Yang, Zhang, et al. (2019)

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5. Applications of microbial carbon capture cell

5.1 Wastewater treatment through different types of PMFC

Energy utilized in wastewater treatment accounts for 3% of the global electricity demand (Saba et al., 2017). Hence, the increasing pressure on energy and treatment systems has led the researchers to identify sustainable technologies to address the challenges faced by the sectors. The BES systems are capable enough to remove 80%−90% COD from wastewater, and this sustainable technology is gaining necessary space among the other advanced wastewater treatment technologies (Ye et al., 2019). A major portion of the organic matter removal occurs at the anaerobic anodic chamber of MCC. The electrogenic bacteria are capable enough to degrade a variety of wastewater including domestic as well as industrial. Around 95% COD removal was attained in a tubular dual-chamber MFC producing a power density of $32W/m^3$ while treating brewery wastewater (Lu et al., 2017). Similarly, the digested swine wastewater (COD over 25,000 mg/L) achieved 91% COD removal and 68% nitrogen removal with a simultaneous power production of $25\ mW/m^2$ (Kim et al., 2020). Apart from huge strength wastewater treatment, MCC is well established in treatment of low strength wastewater as well. More than 80% removal efficiency as obtained in an MFC with *Chlorella* in the cathodic chamber while treating wastewater with a COD of 58 mg/L (Ma et al., 2017).

The addition of microalgae in the cathodic chamber provides multiple advantages of facilitating polishing treatment and value-added product recovery at the cathodic chamber. Microalgae-assisted nutrient removal and recovery in the cathodic chamber has increased the sustainability of BES technology. The posttreatment of a landfill leachate with an ammonium nitrogen concentration of 2537 mg/L in the cathodic microalgal compartment was lowered by 86.3% (Nguyen & Min, 2020). An air lift−type MCC was reported to remove 70.52% of ammonium nitrogen and 69.24% of phosphorus at the cathodic side generating a power density of $972.5\ mW/m^{-3}$ (Hu et al., 2015). Hence, wastewater treatment through continuous mode channeling anodic and cathodic chamber will be capable of providing a complete solution for wastewater bioremediation.

The capability of microalga in heavy metal removal can be an added bonus to the microalgae-incorporated BES. Heavy metal contamination of groundwater as well as river water is one of the growing concerns to human health and environment. On-site remediation of heavy metal−contaminated water has been achieved in river water by the integrating microalgae with sediment MFC. An 82% and 99% removal of zinc and lead was attained even at very low initial concentrations (Kabutey et al., 2019). Apart from this, remarkable removal of Ca, Fe, Mn, Mg, Zn, and Al by *Chlorella* sp. was achieved from municipal wastewater. The residual copper ion after cathodic Cu^{2+} reduction in second chamber was removed via biosorption in the third chamber of a

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triple-chambered algal-based MFC, which increased the copper ion removal efficiency of almost 99.9% (Yang et al., 2021). The salt removal efficiency of microalgae and cyanobacteria has also been experimented upon by researchers. Microalgae *Scenedesmus abundans*—incorporated microbial desalination cell (MDC) has been reported to remove over 55% salt with simultaneous power generation (Ashwaniy & Perumalsamy, 2017).

5.2 Bioenergy generation from MCC

Microalgae-assisted BES can take variety of configurations depending on the placement of microalgae. A biovoltaic cell (BVC) utilizes the external electron generating capability of microalgae through oxidation of organic matter (Wey et al., 2019). On the other hand, an MCC is envisaged to generate metabolic oxygen in the aqueous catholyte to support cathodic reaction alongside carbon capture at the cathodic compartment (Jadhav et al., 2019). Hence, MCC plays a major role among BES systems in generating electrical energy by reducing the energy and cost associated with MFCs. BES with different configuration has been reported to generate power while treating variety of wastewater upon adding microalgae in the cathodic side (Table 9.4).

Apart from bioelectricity, bioenergy in the form of biofuel and biogas can be produced from MCC by effective utilization of the harvested algal biomass. A lipid productivity of 147.6 mg/L.day was attained from green algae *Chlorella vulgaris* with a simultaneous power generation of 5.94 mW/m^3 and at 1292.8 mg/L day CO_2 fixation rate (Li et al., 2019). Similarly, 325 mg/L of biomass *Golenkinia* sp. with 38% lipid was cultivated in a single-chamber algae-assisted MCC, which generated a power density of 6255 mW/m^3 upon treatment of kitchen waste (Hou et al., 2016).

5.3 Valuable recovered from photosynthetic microbes

Value-added products from microalgae have extensive areas of application including pharmaceutical, food, fuel, cosmetics, and so on (Table 9.5). As mentioned earlier, a major feature distinguishing microalgae from other terrestrial plants is its complex biochemical composition as well as low areal requirement for bulk production. One of the major utilities of microalgae in energy sector is via photosynthetic BES, wherein electrical energy is generated with the aid of microalgae incorporated MFCs (Neethu, Tholia, et al., 2020). Apart from this, microalgae on harvesting are a good candidate for production of oils, biodiesel, hydrogen, hydrocarbons, etc., which has attracted the attention of research worldwide. However, equally important recognition has been obtained for the high nutritional value of microalgal species, wherein nutrient and protein supplement is derived from microalgae (Kumari et al., 2023; Ma et al., 2023; Maddiboyina et al., 2023).

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TABLE 9.4 Bioelectricity generation in algae-assisted microbial carbon capture cell.

Substrate used	Reactor configuration	Maximum power density	Cathodic microalgae	References
Synthetic wastewater (SW)	Two-chambered MCC	2.7 W/m^3	*Chlorella vulgaris*	Khandelwal et al. (2018)
Acetate and dairy wastewater	Two chambers PMFC with PBR	2.8 W/m^3	*Chlorella* sp.	Bolognesi et al. (2021)
Dye textile wastewater	Single-chambered PMFC	123.2 mW/m^3	Green algal consortium	Logroño et al. (2017)
SW	Two-chambered MCC	0.85 W/m^2	*Spirulina*	Colombo et al. (2017)
UASB (inoculums) + SW	Two-chambered MCC	158.2 mW/m^2	*Chlorella*	Zheng et al. (2017)
Sediment	Two-chambered MCC	202.9 mW/m^2	*Chlorella*	Zheng et al. (2017)
Artificial wastewater	MBR-MFC	1.2 W/m^3	*C. pyrenoidosa*	Yang et al. (2017)
SW	Two-chambered MCC	6.4 W/m^3	*C. pyrenoidosa*	Jadhav, Ghosh Ray, et al. (2017) and Jadhav, Jain, et al. (2017)
SW	Two-chambered MCC	0.85 W/m^2	*Spirulina*	Colombo et al. (2017)
SW	Two-chambered MCC	0.6 mW/m^2	*C. vulgaris*	Mitra and Hill (2012)
SW	Two-chambered MCC	58.4 mW m^3	*Microcystis aeruginosa*	Cai et al. (2013)
SW	Two-chambered MCC	64.2 mW m^2	*Desmodesmus* sp.	Wu et al. (2014)
Chlorella pyrenoidosa	Two-chambered MCC	2.5 mW/m^2	*C. pyrenoidosa*	Xu et al. (2015)
SW	Two-chambered MCC	187 mW/m^2	*C. vulgaris*	Liu et al. (2015)

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TABLE 9.5 Potential application/value-added derivatives from phototrophs.

Microalgae	Value-added product	References
Chlorella sp.	• Pharmaceutical • Food • Carotenoids	Nabavi and Silva (2018)
Crypthecodinium sp.	• Aquaculture • Food—infant formula	Berzins et al. (2022)
Dunaliella sp.	• Bioactive compounds • Cosmetics • Pharmaceutical • Carotenoids • Food and nutrition	Hosseini Tafreshi and Shariati (2009)
Nostoc sp.	• Food and nutrition • Pharmaceutical	Potts (2000)
Aphanizomenon sp.	• Food and nutrition	Lyra et al. (2001)
Haematococcus pluvialis	• Carotenoids • Astaxanthin	Rizzo et al. (2022)
Arthrospira (Spirulina)	• Food • Cosmetics • Pharmaceutical	Pescosolido et al. (2022)
Nannochloropsis oculata	• Cosmetic	Gkioni et al. (2022)
Spirulina sp.	• Cosmetics, food • Pharmaceutical • Biofertilizer	Reboleira et al. (2019)

Hydrogen is gaining much attention as an alternative to combustible fuels, which is majorly attributed to its carbon free combustion. Direct and indirect photolysis as well as dark and photofermentation are the major mechanisms involved in hydrogen production in microalgae (Sözmen et al., 2022). *Chlamydomonas*, *Botryococcus*, *Scenedesmus*, and *Chlorella* have been reported as promising candidate for hydrogen production (El-Dalatony et al., 2020). *Spirulina platensis* produced 1.92 ± 0.20 mmol hydrogen per gram COD reduced, whereas *Scenedesmus obliquus* was able to generate 56.8 mL hydrogen per gram VS (Batista et al., 2015; Nagarajan et al., 2021). Apart from this, other species including *Anabaena variabilis* (Mona et al., 2020), *S. obliquus* (Florin et al., 2001), *Chlamydomonas reinhardtii* (Rumpel et al.,

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2015), *Platymonas subcordiformis* (Guo et al., 2007), *Tetraspora* sp. *CU2551* (Maswanna et al., 2020), *Lobochlamys culleus* (Ananyev et al., 2009), and *C. vulgaris* (Yun et al., 2014) are capable of hydrogen production.

Carotenoids are compounds capable of fighting issues of medical importance including arthritis, cardiovascular illness, cancer, cataract, premature aging, diabetes, low immunity, etc (Gong & Bassi, 2016; Varela et al., 2015). Owing to the fact that the carotenoid content in microalgae is significantly higher than the green plants, microalgae have been identified as excellent candidate for carotenoid production. *Dunaliella* has gained much attention as algae rich in β-carotene, which is a compound transformed into vitamin A needed by human body as a support to vision and immunity (Ben-Amotz et al., 1991). Certain other microalgae-derivable carotenoid compounds include lutein (Ho et al., 2014), astaxanthin (Suh et al., 2006), free lutein (Prommuak et al., 2013), fucoxanthin (Gómez-Loredo et al., 2016), etc.

The paths opted for processing microalgae to useable energy and marketable fuels majorly depend on the species, growth conditions, and most importantly the lipid content. Low-lipid microalgae are capable of producing heat/power via combustion, synthetic diesel via Fischer−Tropsch synthesis (de Oliveira et al., 2023), and biofuels via pyrolysis or liquefaction (Ağbulut et al., 2023). However, microalgae with high lipid content are capable of producing biodiesel via transesterification on extraction (Thanh et al., 2022) and bioethanol via fermentation process (Kusmiyati et al., 2022). Accumulation of carbohydrate is observed in microalgae when grown under stress. The four times increase in carbohydrate was observed in *C. vulgaris* when subjected to nitrogen stress (Ho et al., 2013). Similarly, *Chlamydomonas reinhardtii*, *spirula*, *C. sorokiniana*, etc. have shown notable increase in carbohydrate content when grown in light limited conditions (Choi et al., 2010). Such cell transformations in microalgae make it an excellent feedstock for bioethanol production. The bioethanol yielding capacity of microalgae is reported to be almost 40 times than those assured by terrestrial crops including corn and beet (Tiwari et al., 2019). Apart from this, utilization of sugar, corn, etc. for biofuel production increases the load on human food chain alongside the high demand for cultivation land.

6. Bottlenecks and future prospective

MCC, which simultaneously takes care of power generation, wastewater treatment, carbon capture, and value-added product recovery from microalgae, is still at the verge of commercialization; however, algae production in an MCC is still too expensive to compete with conventional methods. The complexity observed in taking the technology to industries or common man lies in the higher number of physical components and efficiency determining operating conditions of MCC. The performance of microalgae in terms of oxygen production and carbon capture is one of the significant parameters to

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be focused upon in an MCC. Improving the capacity of oxygen production in microalgae using genetic modification opens a tremendous scope for research in this area. In addition, the possibility of electron generating capacity of microalgae is widely being investigated so as to extract maximum possible output from microalgae to be incorporated in BES. However, the fact that the smaller the size of MFC, the higher the power generation does not sound favorable to algal growth. Cultivation of bulk quantity of algae in MCC implies increase in the volume, which otherwise increases the internal resistance of the system resulting in lower efficiency. This challenge should be addressed by research community by versatile design modifications and modeling. For example, converting an existing algal pond to an MFC will make the system an MCC, which can be easily implementable in industries and STPs.

As discussed in earlier sections on the parameters effecting the performance of MCC, it is evident that the efficiency of the system is species dependent. Above that, the overall system will have to be optimized based on the microalgae employed. Hence, based on the investigations carried out so far on MCC, it will be essential to prepare a thorough guideline stating the species-specific optimum operating conditions of an MCC. Design modification including usage of light filters, immersible anodic chambers, stacked MCCs, etc. can open the path to commercialization of MCC in next to no time. Employing the algal bacterial symbiotic treatment can also open scope to improve the treatment efficiency and algal productivity. In today's decade, clean energy, wastewater treatment, and carbon sequestration have equal demands. An MCC that converts chemical energy present in wastewater to electrical energy by utilizing oxygen produced by microalgae is capable enough to address these challenges. However, research is still needed to make MCC reliable and competing to existing technologies.

7. Conclusion

The chapter has made a critical assessment of various MCCs. Owing to the fact that an MCC is a complex multifunctional system comprising if anaerobic digestion, proton exchange, electron transfer, carbon dioxide generation and capture, microalgal photosynthesis, oxygen production, oxidation, reduction, electrochemistry, and so on, an overview about significant processes are briefed in this chapter. Also, the environmental and commercial benefit of MCC has been discussed through the applications of MCC. The major focus to be laid on for commercialization of MCC lies in optimizing the physical as wee as operating parameters, and this has been indirectly specified by detailing the effect of different factors on the performance of MCC. In addition to this, the bottlenecks and future scope are briefed in the chapter as a guidance to researchers in the field. An MCC is capable of making significant contribution in sustainable socioeconomic development by influencing the overall economics in wastewater treatment and algal production.

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Chapter 10

Desalination through microbial desalination cells and remediation of organic pollutants

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Abstract

Microbial fuel cells (MFCs) utilize microorganisms as biocatalysts, which simultaneously facilitate wastewater treatment and electricity generation. An MFC, which is modified to desalinate brine water, is known as a microbial desalination cell (MDC) in which wastewater treatment, electricity generation, and desalination simultaneously take place by captivating the energy content of wastewater as a resource. In recent times, MDC has proven to be a promising technology for saltwater as well as wastewater treatment. This chapter primarily aims at providing insights into the basic principle of MDCs and their different reactor configurations. Later, an extensive discussion is delivered on the bioremediation of organic pollutants using MDCs.

Keywords

Bioelectrochemical system; Bioremediation; Microbial desalination cell; Organic pollutants; Wastewater treatment.

1. Introduction

Water is an intrinsic part of living. Even though 75% of planet Earth is covered with water, only 3% of it is affordable for safe water consumption. It is estimated that there will be a decline in potable water availability by one-third in the next coming 10 years. Rapid population growth and climate change severely affect the availability of freshwater and cause water scarcity. As a

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result, emphasis is given to utilizing seawater, brackish water, and wastewater for human consumption (Cao et al., 2009; Naha et al., 2020; Sevda & Abu-Reesh, 2017a; Sevda et al., 2014). The existing desalination technologies such as reverse osmosis (RO), multieffect distillation (MED), membrane distillation (MD), and multistage flash distillation (MSF) are highly energy-intensive (6−68 kWh/m^3) (Cao et al., 2009; Imoro et al., 2021). In addition to that, they release greenhouse gases (GHGs) into the environment (Borjas et al., 2017). Recently, membrane desalination (MD) cell, a class of microbial fuel cells (MFCs), has emerged as a promising alternative to former technologies in which desalination and renewable energy (bioelectricity, hydrogen, and methane) generation are simultaneously achieved (Cao et al., 2009; Nayak & Sevda, 2022; Kalankesh et al., 2019). It is reported that, depending on hydraulic retention time (HRT), MDCs can achieve 99% desalination of seawater (Sevda et al., 2015).

The development of MDCs also provided a promising alternative technology for wastewater treatment (Sevda et al., 2015). The bacteria present in an MDC decompose the organic matter and release energy from wastewater. Additionally, they also have the potential for water softening and removal of metal ions from an aqueous medium (Ragab et al., 2019; Sevda & Abu-Reesh, 2017b; Sevda et al., 2013). Thus, MDCs have a great potential to address sustainable development goals (SDGs). From desalination and bioremediation, an MDC offers a solution for SDG 6 (clean water availability) and provides a solution for SDG 7 (clean affordable energy) by generating bioelectricity (Imoro et al., 2021). The particular chapter on MDCs discusses the basic working principle of MDC, its classification, and its role in the bioremediation of organic pollutants present in wastewater along with desalination.

2. Microbial desalination cell: Working principle

An MDC is a bioelectrochemical system (BES) in which electricity is generated by microbial activity. Henceforth, its configuration comprises of elements responsible for all bio- and electrochemical activities. A typical MDC has three chambers: a cathode, an anode, and a desalination chamber. The desalination chamber is separated from anode and cathode by positioning the anion exchange membrane (AEM) and cation exchange membrane (CEM), respectively, on each side (Fig. 10.1). The anodic chamber comprises anode and electrogens, which are also known as anode-respiring bacteria, electrochemically active bacteria, etc (Park et al., 2023). The electrogens are capable of transferring the electrons extracellularly. The bacteria reside on an anode, use organic matter present in wastewater as a substrate for their metabolism, and release electrons, protons, and carbon dioxide through cellular respiration (Tomar et al., 2023). As oxygen is a strong receptor of electrons, an anaerobic condition is maintained in the anode chamber to avoid electron suction by oxygen molecules. Henceforth, the generated electrons will transfer along an

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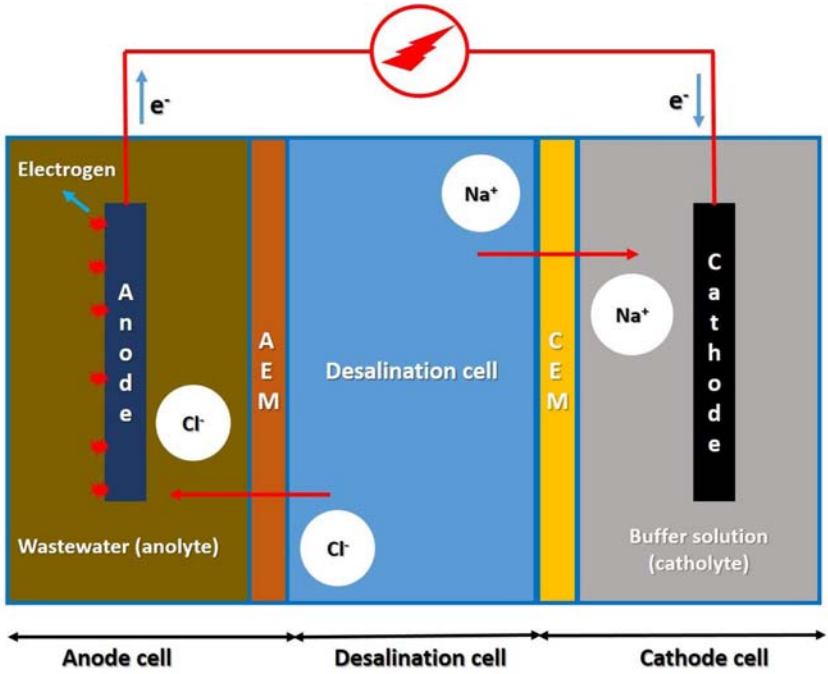

FIGURE 10.1 Conventional three-chambered MDC reactor configuration.

external electric circuit (Cao et al., 2009; Imoro et al., 2021; Sevda et al., 2015).

When electricity is generated on the anode, the positively charged ions (protons, H^+) are released into the anodic chamber, but they are prevented by AEM from leaving the chamber (Jadhav et al., 2022). Thus, it leads to the transfer of negatively charged ions (for example Cl^-) from the desalination chamber toaward anode due to electrophilic attractiveness. Meanwhile, the positively charged ions (Na^+) will transfer toward the cathode cell where they eventually will be reduced. Thus, the transfer of ionic species from the middle chamber leads to the desalination of salt water without an external energy supplement unlike in electrodialysis (Cao et al., 2009; Jatoi et al., 2022). Henceforth, MDCs have been proposed to be a sustainable alternative solution for desalination, wastewater treatment, and clean energy production. Additionally, the recovery of chemicals (ionic species) from the desalination chamber makes the system more fascinating (Jatoi et al., 2022).

The performance of MDCs is generally measured in terms of specific desalination rate (SDR), desalination efficiency, power density, Faradic efficiency, total organic carbon (TOC) removal from wastewater, and pH of the effluent. Nevertheless, The overall performance is significantly governed by various factors such as reactor configuration, conductivity, electrode materials,

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substrates, membranes, HRT, pH imbalance, etc. (Jingyu et al., 2017). However, the upcoming section will primarily focus on various reactor configurations and their respective performances.

3. Types of microbial desalination cells

There are several types of MDCs based on the configuration of reactors. The change in the reactor design is majorly aimed either for salt rejection rate or efficient charge transfer. Table 10.1 summarizes various configurations of MDCs along with their key features and advantages. It is interesting to observe that the efficiency of the cell is considerably influenced by cathodic cell. This dependency is due to the catholyte present in the cathodic chamber in which an electron receptor resides. Henceforth, configurations such as air cathode MDCs and biocathode MDCs are developed. In air cathode MDC, oxygen is used as the ultimate electron receptor, whereas biocathode MDC exploits microbes for catalyzing reduction reactions (Pandit et al., 2023). It is reported that these configurations have enhanced the system performance in terms of reduction potential and desalination. A biocathode MDC will also provide a sustainable solution for the operation instead of pumping air into the system by external source. However, raise in pH anolyte in air cathode MDC and small reduction of bath-mode biocathode cell operation are the major challenges with these configurations (Jatoi et al., 2022; Jingyu et al., 2017; Saeed et al., 2015) (Fig. 10.2).

The electrons produced will not only contribute to electricity generation but also involve in cathodic reactions, which demands more oxidation reactions than the actual requirement for the desalinations. The challenge is overcomed by the development of stack MDCs where multiple ion exchange membranes (IEMs) are inserted between the electrodes. The series of stacks enhances the desalination by facilitating efficient charge transfer across the membranes. Thus, stacked MDCs (SMDCs) produce more energy and cost-effective than other configurations. However, a large number of stacks may cause severe pH imbalances: pH drop in anodic cell affects the microbial activity, and raise in cathodic chamber pH results in remarkable loss in electromagnetic potential (Saeed et al., 2015). A sequential recirculation of electrolytes across the cell can neutralize the pH of electrolytes, which is a creative feature of recirculated MDC (rMDC). Additionally, the performance of the cell also depends on the concentration of buffer solution. It is also reported that rMDCs can produce 33% more power density than the conventional MDCs. However, the recirculation of electrolytes adversely effects the Faradic efficiency of the cell (Luo & Jenkins, 2011). Qu et al. (2012) have addressed the issue by replacing the oxygen at cathode by evolving hydrogen within the chamber.

Likewise, many configurations have been developed to address the challenges posed by conventional MDCs. An upflow MDC (UMDC) is a concentric

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TABLE 10.1 Different configurations of MDCs, their key features, advantages, and challenges.

MDC configuration	Key features	Advantages	Challenges
Air cathode MDC	O_2 as an electron receptor	Higher reduction potential	pH imbalance
Biocathode MDC	Biocatalyzed reduction reactions	Enhanced desalination	Reduction in cell potential
Stacked MDC	Efficient electron transfer	Enhanced desalination	Declined currents due to more compartments
Recirculation MDC	Recirculation of electrolytes	Higher desalination rate and power density	NA
Submerged microbial desalination cell	Integration of desalination and denitrification	No additional energy requirement for denitrification	Scaling up
CMDC	Intensification of MDC with CDI	Less contamination of electrodes	Regeneration of electrodes from ions
Upflow MDC	Concentric tubular cell	Easy to scale up	Drop in pH
Decoupled MDC	Direct insertion of electrodes in salt water	Easy scale up	NA
Osmotic MDC	AEM is replaced by forward osmosis membrane	Low cost Improved performance	Scale up and membrane fouling

Reproduced with permission from Jingyu, H., Ewusi-Mensah, D., & Norgbey, E. (2017). Microbial desalination cells technology: A review of the factors affecting the process, performance and efficiency. *Desalination and Water Treatment, 87*(August), 140–159; Saeed, H. M., Husseini, G. A., Yousef, S., Saif, J., Al-asheh, S., Fara, A. A., Azzam, S., Khawaga, R., & Aidan, A. (2015). Microbial desalination cell technology: A review and a case study. *Desalination, 359*, 1–3.

tubular cell where inner anodic compartment is filled with graphite granules. Graphite granules are well known for providing increased surface area for oxidation reactions, and graphite rods are inserted in the chamber to receive and transfer the electrons to the external circuit. The granule bed is surrounded by an AEM through which Cl^- ions from desalination chamber (outer compartment) are transferred to the anodic cell. The inner layer of desalination compartment is lined with CEM and Pt-C catalyst, and the outer layer of the compartment is

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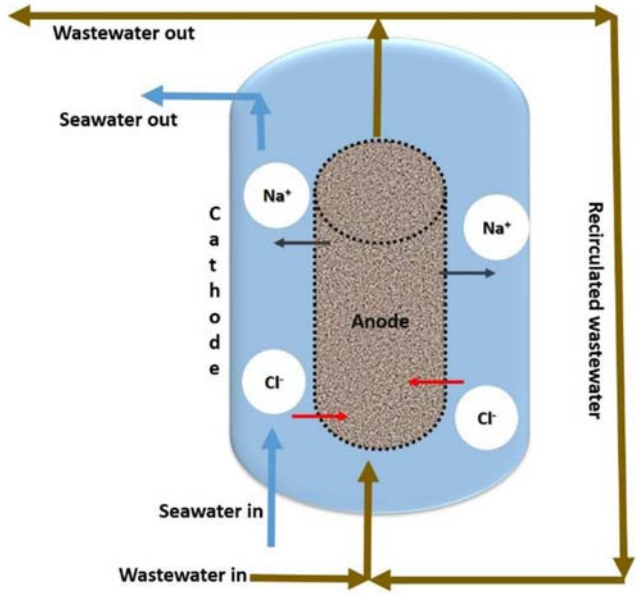

FIGURE 10.2 Schematic representation of upflow microbial desalination cell.

lined with carbon cloth, which acts as a cathode. Thus, there is no requirement for separate cathodic chamber, which made the system compact. The upstream flow through the cell made the system viable on industrial scale (Jatoi et al., 2022). Jacobson et al. (2011) reported that the employment of UMDC before RO system has reduced the capital cost by 22% at the cost of higher HRT, thus leading to the requirement of larger reactor volume.

Another interesting MDC configuration is submerged microbial desalination and denitrification cell (SMDDC). An SMDDC is submerged in groundwater or subsurface water where in situ nitrification, energy generation, and wastewater treatment will occur simultaneously. The two-chambered (anodic and cathodic chambers) cell will be stationed in groundwater, which acts as a desalination chamber. The NO_3^- produced by bacterial metabolism will transfer toward anode. Then, the nitrate containing anolyte will be transferred to cathodic compartment where it will be eventually reduced to N_2 (Zhang & Angelidaki, 2013). Recently, process intensification of MDCs with capacitative deionization is adopted wherein an electrical energy is supplied to electrodes in order to enhance the adsorption of ionic species onto electrodes. However, the potential applied across the cell is about 1.4 V, which can be supported by the MDC. This particular type of cell is known as capacitative MDC (CMDC). The CMDC is reported to be effective in terms of salt, total dissolved solids (TDS), and chemical oxygen demand (COD) removal (Forrestal et al., 2015).

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4. Bioremediation of organic pollutants using MDC

Earlier sections have already laid a foundation for the discussion on remediation of organic pollution using MDCs. It is also discussed that the MDCs can remove COD, TDS, TOC, and fix nitrates from wastewater with different configurations. The bioremediation exclusively takes place in the anodic chamber of an MDC where microbes consume organic matter for its growth and they proliferate. As a consequence, they consume organic pollution from wastewater and additionally generate electricity and does desalination. Sevda et al. (2017) have employed MDCs to treat petroleum refinery wastewater, collected from local effluent treatment plant in Doha, Qatar, and to desalinate real seawater. A maximum of 70.5% COD removal is achieved when initial concentration of salt water is 20 g/L. In this study, acidifying water is used as a catholyte instead of phosphate buffer solution (PBS). It implies that the low pH catholyte favors more electricity generation and salt removal rate. Further, an energy of 32.6 W h/kg COD removal is produced within the cell with a 19.9% desalination efficiency (Table 10.2).

Various investigations have been conducted to develop an alternative for precious Pt-C cathode catalyst, which would decrease the capital cost of the MDC by a greater extent. Elawwad et al. (2020) have developed a novel composite catalyst by anchoring MnO_2 into graphene nanosheets and used for a cathode catalyst in an MDC to degrade synthetic sodium acetate wastewater. The study has found that the catalyst has enhanced COD reduction and improved the Columbic efficiencies. Thus, the developed composite catalyst can be a potential alternative to Pt-C catalyst. In another attempt, microfiltration membrane−coupled biocathode MDC is developed to reduce the capital cost and to enhance over performance. It is found that the process intensification is cheaper than the conventional Pt-C-based MDC reactors. The integrated system is efficient for nutrient recovery and organics removal from domestic wastewater with better desalination and current efficiencies than conventional MDCs (Zuo et al., 2018).

A novel two-chambered tubular MDC is developed to simultaneously remediate organics present in domestic wastewater and to mitigate the pH imbalance in the system. Surprisingly, domestic wastewater without an addition of buffer solution as anolyte significantly balanced the pH in the system and produced a high amount of energy (8 mW). The system, thus, eventually led to 84% removal of COD from domestic wastewater (Jafary et al., 2020). This study again confirms the relationship between pH, charge transfer, internal resistance, energy production, desalination, and wastewater treatment. Addressing the issue of pH imbalances also provided a solution for organics removal from wastewater. As discussed before, CMDCs have proven to be an efficient MDC for desalination and bioenergy production. An extensive research by Forrestal et al. (2015) has also proved CMDC as an effective method for bioremediation of wastewater. The study has efficaciously

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TABLE 10.2 Bioremediation of organic matter from different wastewater using various MDC configurations.

Wastewater	MDC reactor	Innovation	Advantages	References
Petroleum refinery wastewater	Conventional MDC	Acidifying water as catholyte	Increased COD removal Reduction of internal resistance	Sevda et al. (2017)
Synthetic acetate wastewater	Conventional MDC	MnO_2/graphene composite as a cathode catalyst	Improved current generation	Elawwad et al. (2020)
Domestic wastewater	Biocathode MDC	Intensification with microfiltration membrane	Enhanced removal of COD and nutrient removal	Zuo et al. (2018)
Domestic wastewater	Tubular MDC	Two-chambered tubular MDC structure	pH balance, high energy production, and COD removal	Jafary et al. (2020)
Shale gas explosion caused wastewater	CMDC	All the chambers are capable removing organic and inorganic pollutants	High TDS and COD removal and high levels of salt and organics recovery	Forrestal et al. (2015)
Domestic wastewater	rMDC	Reducing pH imbalances using recirculation of electrolytes	pH balance, efficient desalination, and increased power density	Qu et al. (2012)
Synthetic acetate wastewater	Conventional MDC	Improving performance by varying operating temperature	Can be operated at wide range of temperatures	Ragab et al. (2019)
Synthetic acetate wastewater	UMDC	Continuously operating reactor	Higher charge transfer efficiency	Jacobson et al. (2011)
Synthetic acetate wastewater	Microbial electrolysis and desalination cell	Integration of electrolysis and desalination	Concurrent desalination and hydrogen generation	Luo and Jenkins (2011)

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remediated organics present in shale gas–produced wastewater along with desalination. The COD removal and desalination using CMDC have increased by 18- and 5-fold, respectively. The desalination rates are associated with improved conductivity, whereas the improved COD removal, stimulatingly, is associated with COD removal achieved in desalination chamber. It is due to electrochemical-induced adsorption by activated carbon cloths of capacitive deionization (CDI).

An innovative approach of recirculation of electrolytes through desalination cell has boosted power density and extent of desalination when domestic wastewater is utilized as an organic substrate for the bacteria (Qu et al., 2012). The study shows that efficiencies are directly reliant on pH changes. The performance of MDCs is also a function of operating temperature. It is proven that MDCs can be operated at a wide range of temperatures. However, lower temperatures do not encourage the performance of MDCs in terms of COD removal, desalination, and Columbic efficiencies. An increased temperature from room temperature has driven the permeability of CEM; thus, desalination has improved along with COD removal and Columbic efficiency (Ragab et al., 2019).

Process intensification of MDCs is obvious for improved performance. Integration of microbial electrolysis with desalination has substantially increased current density, desalination, and hydrogen production when synthetic sodium acetate wastewater is employed as substrate. However, the performance is inhibited by the accumulation of Cl^- ions in anodic chamber. Henceforth, continuous replacement of wastewater not only improved system performance (Luo & Jenkins, 2011). Even though the study is not directed toward wastewater treatment, it helps to understand how to maintain organic content of wastewater. Similarly, a study conducted by Jacobson et al. (2011) on continuous operation of UMDC with air cathode is also not to comprehend the wastewater treatment using MDCs. However, it figures out to how anolyte can substantially influence the performance of MDCs.

5. Future prospects

It is lucidly understood from the discussion that still there is a great scope for addressing various issues naming from reactor configuration to buffer solution for the betterment of MDC performance. Even though there is a great leap in the advancement of reactor configurations, a compromise exists either between current efficiency and desalination, or desalination and bioremediation, or power density and HRT. Additionally, it is still a great challenge to scale up the reactor configurations. Further, a potential research is required to reduce capital and operational catalyst by replacing precious catalysts and pumping costs in the case of rMDCs and UMDCs. A lack of extensive research in terms of bioremediation of organics is laid a foundation for aspiring researches to explore further.

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6. Conclusion

An MDC is a good example for process intensification, which aims at simultaneous desalination, bioenergy production, ions recovery, as well as wastewater treatment. In terms of footprint area, sustainability, and energy consumption also, an MDC is a great example for process intensification principles. Even though the employment of MDCs, at current stage, cannot replace conventional RO and other desalination techniques, they can be employed as pretreatment for existing desalination systems to reduce energy and capital consumption and to reduce the emission of GHGs.

The development of MDCs has also addressed current severe global issue: wastewater treatment. MDCs have provided sustainable alternative solution for various organic wastewaters as discussed before and laid a foundation for extensive research in this field. However, there still exists a great scope for further research in terms of scale-up, wastewater treatment, replacement of precious catalysts, etc.

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Chapter 11

Bioelectrochemical reduction of heavy metals from industrial effluents

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Abstract
Heavy metal contamination in industrial effluents poses serious threat to the environment and human health. Traditional heavy metal removal techniques, including chemical precipitation and adsorption, are frequently expensive and energy-intensive and produce a lot of chemical sludge. Recent years have seen the emergence of bioelectrochemical systems (BESs), primarily microbial fuel cells (MFCs), as a viable sustainable method for reducing heavy metals from industrial effluents and producing electricity simultaneously. In MFCs, both abiotic and biotic cathodes have demonstrated the ability to remove heavy metals. Biotic cathodes employ microorganisms to facilitate the removal of heavy metals through processes such as biotransformation and bioaccumulation. On the other hand, abiotic cathodes depend on physicochemical mechanisms including adsorption, precipitation, and electrochemical reduction to remove heavy metals from the system. The current understanding of heavy metal removal at abiotic and biotic cathodes in MFCs is highlighted in the chapter. BESs utilize the unique properties of microorganisms and electrochemistry to achieve efficient and environmentally friendly heavy metal removal. The mechanisms underlying heavy metal reduction in BESs, such as microbial metabolism, and electrochemical reduction are discussed. The advantages of BESs include high removal efficiency, low energy consumption, and minimal chemical sludge generation. Overall, this chapter provides a comprehensive overview of the current state of knowledge on heavy metal removal in MFCs and highlights the potential of MFCs as a sustainable and effective technology for addressing heavy metal pollution in wastewater.

a. These authors have equal contribution.

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Keywords
Bioelectrochemical system; Electrodes; Heavy metals; Precious metals; Removal; Wastewater.

1. Introduction

The revolutionary era of industrialization and unplanned urbanization has boosted economical opulence and accelerated the discharge of various inorganic and organic pollutants into aquatic ecosystems. Among the emerging contaminants, the presence of heavy metals in the water bodies has particularly concerned environmentalists due to their biological toxicity and non-degradability (Jacob et al., 2018; Sevda & Abu-Reesh, 2018; Sevda et al., 2017). The most prevalent metallic contaminants include cadmium (Cd), zinc (Zn), selenium (Sn), copper (Cu), nickel (Ni), vanadium (V), chromium (Cr), arsenic (As), lead (Pb), and mercury (Hg), which have the atomic density greater than 5 g/cm^3 and are well known to be toxic, and some of them are carcinogenic (Raychaudhuri et al., 2021). Several industries are responsible for their release in the water reservoirs, for example, wood processing and circuit board manufacturing industries are reported to generate a significant amount of Sn, Pb, Ni, and As contaminated effluents (Hemdan et al., 2021). Other industries such as petroleum refineries, photographic industries, and fertilizer manufacturers are also having a significant impact on increasing heavy metals in the water systems deteriorating the availability of freshwater resources (Sevda & Abu-Reesh, 2017; Sevda & Sreekrishnan, 2014). However, the level of toxicity is proportional to the amount and time of exposure. As per the Environmental Protection Agency's list of priority pollutants, Pb, Cr, Zn, Hg, As, Cd, and Ni are considered a serious threat to both the ecosystem and environment because of their lowest permissible limits and higher health risks among all other metallic pollutants encountered in the environmental samples (Li et al., 2014). The higher solubility of these heavy metals in the aqueous media leads to their absorption and accumulation in the food chain of the biological systems with humans at the top. Once they enter the food chain and their ingestion concentration reaches beyond the objectionable limit, it leads to several serious health disorders ranging from mild (nausea, tiredness) to serious illnesses (cancer). However, the extent of illness varies according to the type of heavy metals and source of contamination. Considering the detrimental effects of heavy metals even in trace amount, it is imperative to remediate metal-contaminated wastewater prior to its discharge back into the environment (Vardhan et al., 2019).

To date, numerous treatment technologies including chemical precipitation, ion exchange, adsorption, coagulation−flocculation, and electrolytic reduction, are reported for eliminating the heavy metals from the contaminated water. These methods of heavy metal removal are expensive, and not eco-

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friendly (in terms of equipment, chemicals used, and amount and nature of sludge generated) (Vardhan et al., 2019). So, it is imperative to look for better techniques, which can be seen in the form of the new and upcoming concept of microbial fuel cell (MFC). It is seen as a promising and well-emerging technology; performing dual functions of wastewater treatment as well as electricity generation by utilizing the natural catalytic/metabolic activity of microorganisms (exoelectrogens) (Kaushik & Singh, 2020). In the simplest form, MFC consists of anodic and cathodic compartments with a proton exchange membrane (PEM) for separation between them to avoid the migration of electrolytes between the two chambers (Ha et al., 2024). The basic procedure involved in the working of MFC is that during the substrate oxidation at anode using bacteria (exoelectrogens), electrons and protons are generated and electrons travel from anode to cathode via an external circuit, whereas the protons generated/produced from the anaerobic oxidation diffuse through the PEM to reach cathode compartment, where heavy metals are removed/reduced and also electricity is produced. Basically, oxidation reactions take place at the anode and reduction occurs at the cathode (Nancharaiah et al., 2015). In comparison with old conventional technologies, MFC is eco-friendly and facilitates the direct conversion of substrate's chemical energy into electricity and also, safe and quiet in performance/functioning. In addition, we can observe 50%−90% less solids generation, which is to be disposed of (i.e., sludge), and also sludge produced is way more stable as compared with the sludge produced in the conventional wastewater treatment process. Moreover, integration of MFCs with other technologies such as plant MFCs can enhance heavy metal removal efficiency and overall system performance (Kuleshova et al., 2022). In this chapter, we have provided an overview of the current research on heavy metal removal in MFCs, including the mechanisms involved, the factors influencing the performance of MFCs for heavy metal removal, and the challenges and opportunities for future research in this field. The understanding of heavy metal removal in MFCs can contribute to the development of sustainable wastewater treatment technologies that not only generate electricity but also effectively remove heavy metals from wastewater, thereby mitigating their negative impacts on the environment and human health.

2. Heavy metals in aquatic environment

Heavy metals occur naturally owing to various natural processes such as bedrock weathering while anthropogenic source of heavy metals includes mainly industrial wastewater discharge. Untreated/partially treated industrial effluents discharged into the water bodies can be responsible for toxic effects on aquatic flora and fauna. Various industries that are responsible for heavy metal effluents generation include leather tanneries, pulp-paper industries, textile industries, pesticide and fertilizer industries, electroplating industries,

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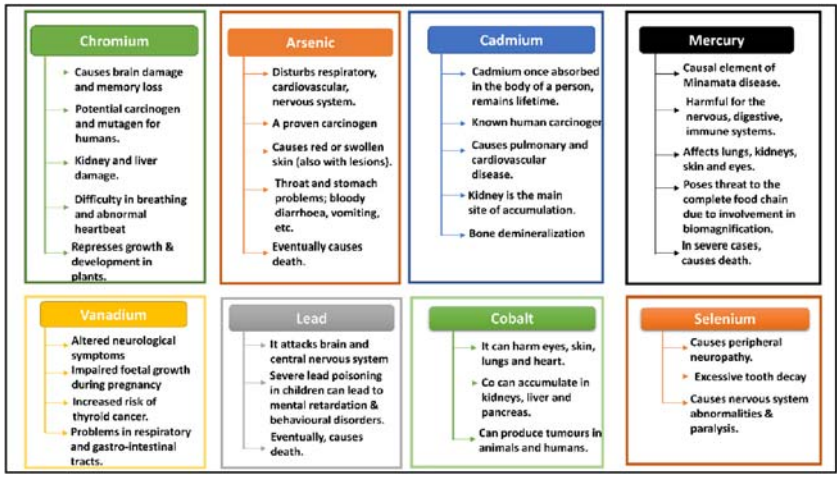

FIGURE 11.1 Detailed description on effect of heavy metals on human health.

mine extraction, smelting industries, chemical manufacturing industries, and many more. Other minor sources include medical applications and household practices (Zhou, Yang, et al., 2020; Zhou, zhang, et al., 2020). In aquatic bodies, these heavy metals tend to accumulate and are responsible for biomagnification (i.e., increased concentration of the toxicant at successive trophic level of the food chain). Other effects of heavy metals in the aquatic environment include the uptake by aquatic organisms through gills, adsorption or binding on the surface, and afterward, intracellular transport causing heavy metal toxicity (Baby et al., 2011).

In minimal amount, heavy metals are essential for living organisms, whereas the excess quantities of heavy metals cause toxicity and are fatal to the biota. Because of their bioaccumulative nature, nonbiodegradability, they pose threat to the environment as well as the living organisms. Also heavy metals are known to be carcinogenic, mutagenic, and teratogenic in nature (Mathuriya & Yakhmi, 2014). Cardiovascular abnormalities, respiratory troubles, Minamata disease (caused by mercury poisoning), problems with the gastrointestinal tract, lungs, and kidneys, malignancies of various organs, and skin cancer are some of the effects of heavy metals on living organisms. Fig. 11.1 provides comprehensive details on major effects of several heavy metals on humans.

3. Bioelectrochemical system

Bioelectrochemistry is emerging as a rapidly growing field exhibiting its notable potential in converting the energy present in wastewater to value-added products such as biofuels, hydrogen, nutrients, heavy metals,

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bioelectricity, etc. (Jadhav & Chendake, 2019). It offers an eco-friendly, economic, and sustainable alternative to meet the energy demands raised due to tremendous population growth. In principle, the microorganisms present at the anode act as a biocatalyst, which facilitates the oxidation reaction generating electrons and protons, which are consumed during reduction reactions at cathode. The membrane separating the anodic and cathodic chambers not only restricts the intermixing of electrolytes but also helps in maintaining the electroneutrality inside the electrochemical cell. Bioelectrochemical system (BES) can be categorized mainly as MFCs, microbial electrolysis cells (MECs), and microbial desalination cells (MDCs) (Gul & Ahmad, 2019). In MFCs, exoelectrogens oxidize organic matter at the anode, generating electrons that can then flow through an external circuit to the cathode (Eq. 11.1). At the cathode, these electrons are used to reduce terminal electron acceptors (TEAs) such as O_2, CO_2, and heavy metals (Eq. 11.2) (Fig. 11.2). From thermodynamic point of view, the redox reactions occurring in MFC result in a positive overall cell potential (E^0_{cell}) and a negative Gibbs free energy (ΔG^0), which indicate a thermodynamically feasible and spontaneous reaction (Hamelers et al., 2010). Various configurations of MFC can include (1) single-chambered MFC (constitutes single anode chamber and open-air cathode); (2) double-chambered MFC (constitutes two chambers, i.e., anode and cathode chamber separated by a proton exchange membrane); (3) stacked MFC (MFC units arranged in stacks, either in series or parallel circuit connections); and (4) microsized MFC (constitutes of smaller-sized units/reactors) (Rao, Varshney, et al., 2023). The inexorable heavy metals contamination requires an immediate attention and effective treatment. In recent years, BESs have shown an incredible potential in the removal and recovery of heavy metals from

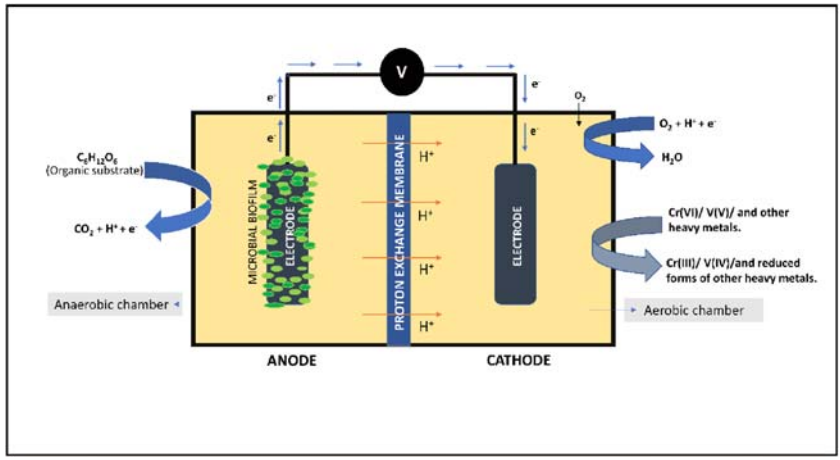

FIGURE 11.2 Microbial fuel cell architecture and functioning.

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wastewater. The reduction of heavy metals can be achieved either in MFC or MEC mode depending on the type of metallic ion and corresponding cell potential (Jadhav et al., 2021). If the reduction potential of the metals at the cathode is higher or more positive than the oxidation potential of the electron donor at the anode, it creates a positive cell potential, leading to a spontaneous reaction in MFC mode operation. For example, heavy metals, i.e., Cr(VI) ($E^0_{red} = 1.33V$ vs. SHE), Hg(II) ($E^0_{red} = 0.91V$ vs. SHE), and Cu(II) ($E^0_{red} = 0.28V$ vs. SHE) have a positive reduction potential, which is way higher than the oxidation potential of acetate ($E^0_{ox} = -0.289V$ vs. SHE) and therefore results in the thermodynamically feasible and spontaneous reduction of these ions in MFCs (Eq. 11.3) (Mathuriya & Yakhmi, 2014). On the other hand, heavy metals such as Ni, Pb, and Cd have a lower or negative reduction potential, when compared with the acetate oxidation potential at the anode. Hence, external energy is necessary to facilitate the reduction of metals at the cathode of MECs. Typically, cathodes play a vital role in heavy metal removal, involving abiotic processes, which could be (1) reduction at the cathode and (2) deposition at the cathode surface. Biotic cathode if used can aid in bio-reduction, bioaccumulation, biosorption, and biomineralization (Ezziat et al., 2019). However, some studies have also attempted the removal of heavy metals in an anode chamber of microbial fuel cell using the bioremediation ability of microorganisms present.

Anode reaction:

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^- \quad (11.1)$$

Cathode reaction:

$$6O_2 + 24H^+ + 24e^- = 12H_2O \ (E^0 = 1.23\ V) \quad (11.2)$$

In case of heavy metals reduction (chromium)

$$Cr_2O^{2-}{}_7 + 14H^+ + 6e^- = 2Cr^{3-} + 7H_2O \ (E^0 = 1.33\ V) \quad (11.3)$$

4. Metal removal mechanisms in bioelectrochemical system

Heavy metals pose threat to the environment and human beings due to their extreme toxicity, carcinogenicity, and nonbiodegradability (Mathuriya & Yakhmi, 2014). Heavy metals present in water bodies affect aquatic life, components of the food chain, and the esthetics of the water body. So, there is an urgent and inevitable need for treating industrial effluents before discharging them into the water bodies. Conventional methods for wastewater treatment are expensive and non-eco-friendly and thus have to be replaced with other sustainable techniques such as MFCs, a BES, which work in favor of metal removal and recovery (Wang & He, 2020). It is an environmentally

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friendly and promising technology that utilizes microbe's electrocatalytic machinery for the removal/reduction/recovery of heavy metals (from industrial wastewater) as well as aids in electricity generation (Jadhav et al., 2017, Jadhav, Park, et al., 2022, Jadhav, Chendake, et al., 2022b). Basically, the cathode plays the main role in metal removal/reduction/recovery, which can be of two types: abiotic cathode and biotic cathode (discussed in later parts). Abiotic cathodes are the catalysts or mediators for electrons, which can perform reduction and deposition of heavy metals, whereas biotic cathodes can perform other functions such as bioaccumulation, bioreduction, biosorption, and biomineralization (Ezziat et al., 2019). Wang and He (2020) described four primary techniques for metal removal, which include direct redox reaction, indirect by-product precipitation, ion migration, and biological removal (Mathuriya et al., 2018). Among these, direct redox reaction is the most commonly reported mechanism for metal removal in MFCs and MECs, which are typical types of BESs, whereas bioaccumulation, biosorption, and intracellular or extracellular biological reduction are the basic methods of biological elimination of heavy metals in both anodes and cathodes of MFCs. Zhang et al. (2015) demonstrated stacking of Cr(VI) and Cu(II) reducing MFCs to self-power an MEC for simultaneous and selective reduction of Cr(VI), Cu(II), and Cd(II). Jiang et al. (2020) developed a novel microbial metal enrichment and recovery cell achieving above 95% removal of Cu(II) and Cd(II) via ion migration and subsequent electrochemical reduction in the cathode. Here, metal ion migration has resulted from the anode chamber to the cathode chamber by the action of generated electricity, which is subsequently reduced in the cathode chamber. The basic and most commonly used method for heavy metal removal in MFCs is the reduction at the cathode. Most of the studies have demonstrated the same (Kumbhar et al., 2021). Overall, the heavy metal removal mechanisms in MFCs are complex and can involve multiple processes. The specific mechanisms may vary depending on the types of microorganisms, heavy metals, and operating conditions in the MFC system. Further research is needed to better understand these mechanisms and optimize MFCs for heavy metal removal applications.

5. Metal removal using abiotic cathode electrodes

The most common type of MFCs used for heavy metal removal/recovery consists of a biotic anode for anaerobic degradation of organic matter generating electrons and protons and an abiotic cathode for reduction of heavy metal by accepting the anodic products (electrons and protons). Abiotic cathodes are commonly used for reducing various heavy metals in both single-chambered and double-chambered MFCs. The pioneering work of Wang et al. (2008) demonstrated the feasibility of simultaneous power generation and Cr(VI) reduction at the cathode in microbial fuel cells. It took 150 h (pH 2) for the two-chambered MFC to fully reduce 100 mg/L Cr(VI) from synthetic wastewater. In

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addition, a voltage of 0.91 V and a power density of 150 mW/m^2 were produced utilizing 200 mg/L Cr(VI) as an electron acceptor. Cr(VI) reduction at the abiotic cathode is a pH-dependent process, and it is more favorable when the pH is lower. Gangadharan and Nambi (2015) extensively studied the effect of pH on Cr(VI) reduction at abiotic cathode by varying the catholyte pH from 2 to 9 in their double-chambered MFCs, and they observed negligible chromium reduction at pH 7 and 9, whereas, at pH 2, almost 98% chromium was reduced within 48 h, which was attributed to increasing in oxidation reduction potential (ORP) value of Cr(VI) solution with a decrease in pH value, which was 540 mV at pH 2, while it reduced to 270 and 139 mV at pH 7 and 9, respectively. A conductive polymer called polypyrrole (PPy) was used to facilitate the transfer of electrons from the cathode to Cr during an attempt to reduce Cr(VI) at neutral pH condition, and nanowire structured PPy/9,10-anthraquinone-2-sulfonic acid sodium salt (AQS)—modified cathode demonstrated high removal rate for Cr(VI) (100% elimination of 20 mg/L Cr(VI) within 46h) and high power output (299.6 mW/m^2). The conductive polymer dissolving in numerous batch tests as well as Cr(III) attaching on the electrode surface posed limitations on the system's durability and practicality for real-time application for wastewater treatment in the study (Pang et al., 2013).

With an initial concentration of 204 ppm, 99.5% of the Cr(VI) from real electroplating wastewater was removed by reducing $Cr_2O_7^{2-}$ to Cr_2O_3 and forming precipitates at the cathode electrode. Li et al. (2008) attained a power density of 1600 mW/m^2 at an ideal pH of 2.5. Aiming for a sustainable approach, Singhvi and Chhabra (2013) investigated the utilization of algal biomass as an easily accessible substrate in the anodic chamber. The MFC produced 207 mW/m^2 power density and removed 98% of Cr(VI) within 96 h at pH 2 using algal biomass at anode electrode. Recently, Yang et al. (2022) developed a photocatalysis-integrated MFC for enhanced chromium reduction wherein MXenes-modified photocathode was utilized in a double-chambered MFC for chromium reduction. The photocathode-based MFC achieved 72.84% chromium reduction in 72 h as compared with 60.45% removal in unmodified MFC, and the power output was also 41.95% higher than the unmodified cathode MFC, thus presenting a new avenue of research to explore the integrated photocatalysis and MFC systems with different new photocatalysts present to simultaneously treat the wastewater and energy generation.

6. Metal removal using biocathode electrodes

The application of biocathode in MFCs has been demonstrated in numerous studies with higher cathode potential for enhanced oxygen reduction reaction (ORR), biosensor application, bioremediation, and resource recovery (Huang et al., 2011). Additionally, the use of biocathode in MFCs has established benefits with low operational cost, enhanced cathodic reactions, and high-power output. Biocathode in MFCs can be both aerobic or anaerobic.

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Despite being noted benefits, the number of studies on metal removal/recovery in biocathode MFC is very limited (Ezziat et al., 2019). Chemical reduction of heavy metal by accepting electrons and protons generated at the anode is a major metal removal mechanism in the case of abiotic cathode, whereas with biotic cathode, metal removal is enhanced through biosorption, biotransformation, precipitation, and microbial uptake (depicted in Fig. 11.3). Initial efforts for heavy metal removal in biocathode of MFC were done by Tandukar et al. (2009); their study demonstrated the improved Cr(VI) removal in biocathode MFC with a high removal rate of 0.46 mg Cr(VI)/gVSS.h along with power generation of 55.5 mW/m^2. The study also reported the presence of putative Cr(VI) reducing microbial communities in cathodic biomass, which are responsible for enhanced metal removal. Later on, an innovative approach was adopted by applying electrode inversion for metal removal at the cathode for which an already acclimatized electrode with exoelectrogenic biofilm was used as a biocathode for Cr(VI) reduction. The electrode inversion methods have led to 2.9 times higher Cr(VI) reduction majorly due to the development of higher bacterial biomass at inverted electrode having both exoelectrogenic and exoelectrotrophic bacteria (Wu et al., 2015). Singh and Kaushik (2021) in their study demonstrated the use of wetland soil inoculum to develop both bioanode and biocathode of MFCs for removal of low redox potential heavy metals (Cd and Ni). Their results interestingly showed significant difference in microbial community development at anode and cathode despite using same inoculum along with high metal removal efficiency. The bacteria present in the cathode chamber play a significant role in the removal of metals by either adsorbing the metal ions to their outer membrane or utilizing the metals as a

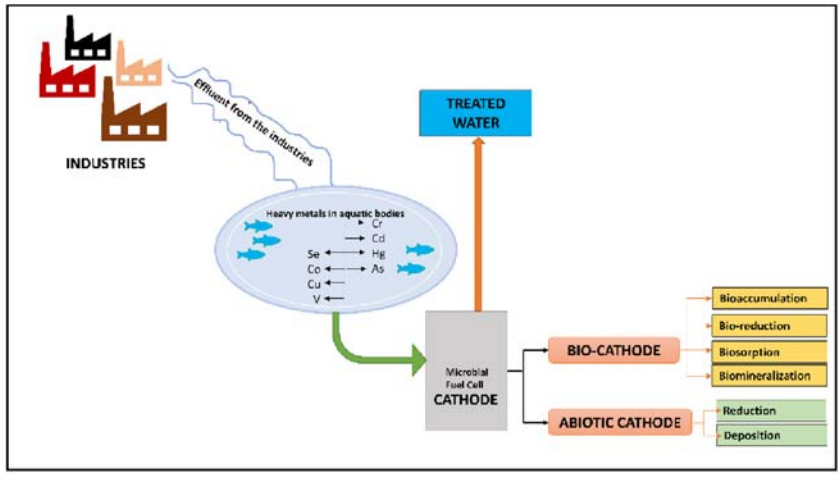

FIGURE 11.3 Schematic representation of industrial effluent treatment at the cathode in microbial fuel cells.

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nutrient source. This bacterial activity contributes to the overall effectiveness of metal removal in the system (Kaushik & Singh, 2020). The diagram (Fig. 11.3) illustrates some processes followed by biocathode microbial biofilm for heavy metal removal. Vanadium removal and power production utilizing biotic and abiotic cathodes in MFC were compared by Qiu et al. (2017), who found that biocathode MFC had improved vanadium removal majorly due to efficient electron transfer that was augmented by bacteria. In MFC with a biocathode, power density was also 10% greater than in MFC with an abiotic cathode. The improved performance of biocathode MFC was attributed to the emergence of *Dysgonomonas* and *Klebsiella* genera in biocathode responsible for high vanadium removal and electricity generation, respectively. To improve the strong biofilm attachment on the cathode electrode, Wu et al. (2016) used ex situ acclimatization of biocathode and NaX-zeolite modification on the cathode electrode, which improved the Cr(VI) removal and power output by 1.7 and 8.2 times, respectively. In another study, biocathode modified with amino-functionalized carbon nanotubes showed good biofilm attachment and enrichment of chromium reducing bacteria on the modified cathode, which resulted in 2.06 times higher metal removal by modified cathodes (Yu et al., 2022). In a recent study, nano-FeS electrode biofilm was first developed at the anode in double-chambered MFC, which, later on, was utilized to function as a biocathode for Cr(VI) reduction. The synergy of nano-FeS and active biofilm formation led to high power output (40.75 mW/m^2) and chromium removal rate (3.99 mg/L/h) (Zhuang et al., 2023). Electrode inversion and electrode acclimatization have been demonstrated to enhance the performance of the biocathode in numerous investigations on biocathode MFC, which exemplify the role of a mature biofilm in achieving high metal removal efficiency. Also, another way of achieving good biofilm formation can be through cathode modification with high surface area and biocompatible materials.

7. Removal of heavy metals from industrial wastewater using bioelectrochemical system

Typical sources of heavy metal pollution include electroplating industries, leather tanneries, chemicals, textiles, paper and wood processing, and other craft industries. Heavy metal−generating industries are generally categorized under the red category. So, it is inevitable to treat these effluents before discharging them into the water bodies. Specifically, electroplating industries discharge toxic heavy metals such as chromium, cadmium, and nickel (Ahmad et al., 2020). Kim et al. (2017) focused on the electroplating hexavalent chromium wastewater treatment using MFC. The study emphasized on the increased efficiency of chromium reduction as well as power generation with the use of bipolar membrane (BPM) as compared with the PEM-MFC. The study shows maximum power density of PEM-MFC (47.2 mW/m^2), while

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significantly higher power densities were observed with BPM-MFC (150.5 mW/m^2) with 50% chromium wastewater. In a recent study conducted by Karuppiah et al. (2022), electroplating industry effluent, which is known for its high organic content (COD ~2500 mg/L), was utilized as a substrate for electroactive bacteria in the anode chamber of an MFC. The MFC demonstrated an impressive power output of 260 mW/m^2 and achieved a total COD removal of 87% during the experiment. This highlights the potential of utilizing electroplating industry wastewater as a viable substrate for energy and power generation in MFCs, whereas effluent could be acidic, which needs to be adjusted to neutral (pH~ 7) before treatment in MFCs. Acid mine drainage and municipal wastewater cotreatment were demonstrated by Vélez-Pérez et al. (2020) showing the removal efficiencies of Cd, Cu, Fe, Al, Pb, and As 42%, 84%, 71%, 77%, 55%, and 42%, respectively. Also, the maximum power density was observed to be 14,000 mW/m^3 using hazardous effluent. Wu et al. (2020) depicted Cr(VI) removal rate from wastewater as high as 4.07 mg/L/h and power density of 309.34 mW/m^2 with modification of cathode with multiwalled carbon nanotubes and biogenic gold nanocomposite. The high chromium removal rate can be attributed to the increased electrical conductivity and electrocatalytic activity of the modified cathode. Miran and Waseem (2021) established that the complex waste acclimatized culture is better than the nonacclimatized one in terms of bioelectricity generation utilizing the tannery wastewater. An enhanced power density was observed in acclimatized culture (223 mW/m^2) and, around 143 mW/m^2 in the nonacclimatized culture. Tao et al. (2014) focused on heavy metals removal from fly ash leachate using a combined BES and electrolysis approach, and observed high removal efficiencies. Specifically, Cu(II), Zn(II), and Pb(II) showed removal efficiencies of 98.5%, 95.4%, and 98.1% respectively, indicating the potential effectiveness of the approach for heavy metal removal from fly ash leachate. More and Gupta (2021) demonstrated 87.88% of Cr(VI) removal in 24h at an influent concentration of 50 mg/L of electroplating industry effluent. Zhou, Yang, et al. (2020) have developed a novel biochar material from the industrial paper sludge doped with nitrogen for MFC cathode fabrication for reducing Cr(VI) to Cr(III). With enhanced electrocatalytic activity and large surface area, this system achieved 55.1% reduction efficiency, whereas 41.8% chromium reduction was observed when no nitrogen doping was done in prepared biochar. Lee et al. (2023) depicts the utilization of *Pseudomonas aeruginosa* and electrically conducting wall for removal of chromium from industrial wastewater effluents; maximum current density produced was around 11.2 A/m^2, with the removal efficiency of 99.6% from 100 mg/L initial concentration removing 2.49 mg/L/d of Cr(VI). Use of biotic cathode in MFC can be seen as viable option to enhance the heavy metal removal efficiencies and also to treat heavy metals with low reduction potential efficiently. Table 11.1 lists various studies involving removal of heavy metals in microbial fuel cells.

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TABLE 11.1 Studies on heavy metal removal in biotic and abiotic cathode MFCs.

Sr. no.	MFC type	Electrode material	Cathode type	Heavy metal	Removal	Maximum power output	References
1	Single-chamber MFC	Anode: carbon brush Cathode: carbon cloth/Pt coated	Biotic	Cu(II)	98.3%	10.2 W/m^3	(Wu et al., 2018)
2	Double-chamber MFC	Anode: carbon felt Cathode: carbon cloth	Abiotic	Cr(VI)	100%	1221.91 mW/m^2	(Li et al., 2018)
3	Single-chamber MFC	Anode: carbon cloth Cathode: carbon cloth/Pt coated	Abiotic	Cd(II)	90%	3.6 W/m^2	(Abourached et al., 2014)
4	Double-chamber MFC	Anode: graphite felt Cathode: carbon paper	Abiotic	Hg(II)	99.54%	433.1 mW/m^2	(Wang et al., 2011)
5	Double-chamber MFC	Anode: carbon brush Cathode: carbon cloth	Abiotic	Ag(I)	99.92% (recovery)	4.25 W/m^2	(Choi & Cui, 2012)
6	Double-chamber MFC	Anode: carbon brush Cathode: carbon cloth	Abiotic	Au(III)	99.89% (recovery)	6.58 mW/m^2	(Choi & Hu, 2013)
7	Double-chamber MFC	Anode: graphite plate Cathode: graphite plate	Abiotic	Cr(VI)	100%	150 mW/m^2	(Wang et al., 2008)
8	Double- chamber MFC	Anode: graphite gate Cathode: graphite foil	Abiotic	Cu(II)	99.88% (removal) 84% (recovery)	0.80 W/m^2	(Heijne et al., 2010)

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9	Double-chamber MFC	Anode: carbon fiber felt Cathode: carbon paper	Abiotic	As(III)	100%	752.6 mW/m^2	(Li et al., 2016)
10	Double-chamber MFC	Anode: carbon fiber felt Cathode: carbon fiber felt	Biotic	V(V)	60.7%	529 mW/m^2	(Qiu et al., 2017)
11	Double-chamber MFC	Anode and cathode: graphite material	Abiotic	Hg(II)	98%	32.6 mW/m^2	(Kumar et al., 2020)
12	Double-chamber MFC	Anode: carbon felt Cathode: carbon felt fabricated with strain LZU47-1	Biotic	Cr(VI)	98.63%	252.36 mW/m^2	(Zhao et al., 2021)
13	Double- chamber MFC (BPM)	Anode: carbon paper Cathode: carbon paper	Abiotic	Cr(VI)	53.1%	150.5 mW/m^2	(Kim et al., 2017)
14	Double-chamber MFC	Anode: carbon felt Cathode: platinum coated carbon cloth	Abiotic	Cu(II)	>98%	224.1 mW/m^2	(Miran et al., 2017)
15	Double-chamber MFC	Anode: graphite plates Cathode: graphite plates	Abiotic	Cu(II)	>99%	339 mW/m^3	(Tao et al., 2011)
16	Double- chamber MFC	Anode: carbon fiber felt Cathode: carbon fiber felt	Abiotic	V(V)	25.3%	572.4 mW/m^2	(Zhang et al., 2009)
17	Double-chamber MFC	Anode: graphite plate Cathode: graphite plate and granules	Biotic	Cr(VI)	2.4 mg/ g.VSS/h	2.4 W/m^3	(Huang et al., 2010)
18	Double- chamber MFC	Anode and cathode: carbon cloth	Abiotic	Cr(VI)	100%	767 mW/m^2	(Gangadharan & Nambi, 2015)

Continued

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TABLE 11.1 Studies on heavy metal removal in biotic and abiotic cathode MFCs.—cont'd

Sr. no.	MFC type	Electrode material	Cathode type	Heavy metal	Removal	Maximum power output	References
19	Double-chamber MFC	Anode and cathode: graphite plates	Biotic	Cr(VI)	100%	55.5 mW/m^2	(Tandukar et al., 2009)
20	Double-chamber MFC	Cathode: carbon material	Abiotic	Cr(VI)	2.13 $g/m^3/h$	1540 mW/m^2	(Gupta et al., 2017)
21	Double-chamber MFC	Anode: graphene derivative (L-GO/ZnO)	Abiotic	Pb(II)	91.07%	1350×10^{-3} mW/m^2	(Yaqoob et al., 2021)
22	Double-chamber MFC	Anode: graphene derivative (L-GO)	Abiotic	Pb(II)	85%	20×10^{-3} mW/m^2	(Yaqoob et al., 2021)
23	Double-chamber MFC	Anode: graphite brush Cathode: graphite brush	Biotic	Cd	87%	722 mW/m^2	(Singh & Kaushik, 2021)
24	Double-chamber MFC	Anode: graphite brush Cathode: graphite brush	Biotic	Ni	92%	722 mW/m^2	(Singh & Kaushik, 2021)

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8. Practical implications and prospects

Heavy metal pollution is a significant environmental issue that poses risk to human health and ecosystems. Industrial activities, agricultural runoff, and improper waste disposal are some of the main sources of heavy metal contamination in natural environments (Sharma et al., 2023). Traditional methods for heavy metal removal such as chemical precipitation and adsorption can be expensive, energy-intensive, and produce toxic sludge as a by-product. However, application of MFCs looks promising and sustainable and has shown great potential for heavy metal removal and recovery, offering practical implications for addressing heavy metal pollution. But before this technology can compete on a commercial basis, several issues need to be resolved. The primary focus of the research must be on the development of new, commercially viable electrode materials with large surface area and high conductivity to encourage the growth of microbial biofilms with reduced charge transfer resistance, low-cost proton exchange membranes (Rao, Kaushik, et al., 2023), modification techniques, and the production of high areal current densities. One of the challenges faced in MFCs is the limited efficiency in reducing metals with low redox potential, due to their lower capacity for accepting electrons. To address this issue, a potential solution highlighted in the study Singh and Kaushik (2021) involves the use of biocathodes, where microbial communities developed at biotic cathode act as biocatalysts. These microbial communities play a crucial role in the reduction and recovery of metals in MFCs, while also offering potential cost reduction benefits by eliminating the need for expensive catalysts and oxygen supply in the cathode. Synergistic approaches involving combining MFCs with other technologies such as constructed wetlands could create synergistic effects, resulting in more efficient heavy metal removal (Wang et al., 2022). Moreover, MFCs have the ability for resource recovery in the form of metals and to recover energy in the form of electricity from hazardous metal-laden wastewater, while simultaneously treating waste and recovery energy that makes MFCs the future ready technologies in line with the circular economy concept. In the future, MFCs could be integrated into wastewater treatment plants to not only remove/recover heavy metals but also generate electricity (Jadhav et al., 2024), thereby providing a sustainable approach to heavy metal removal with the added benefit of resource recovery (Hemdan et al., 2022).

9. Conclusion

In conclusion, MFCs have shown significant potential as a sustainable technology for heavy metal removal from wastewater. Both abiotic and biotic cathodes in MFCs have demonstrated effective heavy metal removal capabilities. Abiotic cathodes offer advantages such as high removal efficiency

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and stability but may require additional chemical inputs and can face challenges with fouling and regeneration. Biotic cathodes, on the other hand, leverage the metabolic capabilities of microorganisms for heavy metal removal, which can potentially enable resource recovery but may face challenges related to microbial diversity, stability, and scalability. Further research is needed to better understand the underlying mechanisms of heavy metal removal in MFCs, optimize operational conditions, and explore potential synergistic effects between abiotic and biotic processes. Long-term monitoring and evaluation of the environmental impact of heavy metal removal in MFCs are crucial for assessing their practical applicability and sustainability. Overall, heavy metal removal in MFCs represents a promising approach to addressing heavy metal pollution in wastewater, with the potential for simultaneous energy production and environmental remediation. Further advancements in MFC technology, coupled with a thorough understanding of heavy metal removal mechanisms, can pave the way for the practical implementation of MFCs as an effective and sustainable solution for heavy metal removal in wastewater treatment. The ability of MFCs to remove almost 70%−100% of certain heavy metals, along with the added advantage of recovering economically important heavy metals, makes them a promising alternative to conventionally used methods.

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Chapter 12

Microbial electrosynthesis of fatty acids and industrial chemicals through carbon sequestration

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Abstract

Microbial electrosynthesis (MES) is one such embryonic technology that stands out because of its purely biotechnological and sustainable approach toward decarbonization of the environment with concomitant valuable product recovery. The synthesis of organic compounds using MES is an effective method for producing a variety of beneficial products (acetate, butyrate, ethanol, methane, etc.) as well as for reducing the load of CO_2 on the environment to mitigate the detrimental effects of greenhouse gases such as global warming and climate change. This technology can also abet in storing excess renewable electrical energy in the form of chemical C−C bonds, thus mimicking photosynthesis. In this veneration, this chapter discusses the various biocatalysts employed, products recovered, the product purification strategies, the scale-up attempts of MES, and bottlenecks that need addressing to expedite the commercialization of this technology and will also discuss its potential to transform into a revolutionary sustainable technology.

Keywords

Acetic acid; Biocathode; Bioelectrochemical system; Biofuel; Carbon sequestration; Microbial electrosynthesis.

1. Introduction

Amid industrial advancements, the increased carbon emissions have had adverse effects on the global environment and climate (Yadav et al., 2021). In

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this regard, carbon sequestration is a process that helps in reducing the impact of these emissions on the atmosphere by stabilizing and storing carbon in both solid and dissolved forms, formally known as carbon capture and utilization (CCU). Microbial electrosynthesis (MES) is one such CCU technique where biosynthesis of commodity chemicals can be achieved through CO_2 fixation with the help of electrical energy. This technology holds great potential of reducing the carbon footprint and is well aligned with sustainable development goal 13, which focuses on combating climate change. The electricity required for MES can be provided by renewable technologies such as solar energy, wind energy, etc. or excess off-grid power, thus rendering sustainability to the technology. The technology of MES can absorb and fix carbon dioxide, which reduces the greenhouse impact and promotes decarbonization. Further, MES has also been recognized as an effective technique to store electrical energy from renewable sources in the form of chemical compounds since the power produced by these renewable sources is typically intermittent, and thus, excess power can be stored in C−C bonds of organic chemicals via MES (Rovira-Alsina et al., 2021). Further, MES is an emerging technology, which can produce a variety of high value-added chemical compounds such as acetate, methane, and other organic acids with the supplementation of a minute amount of external electricity, which is required to make the reaction thermodynamically feasible. Although MES technology has many advantages, there are certain challenges (i.e., low product yield and inconsistent performance, etc.) that still need to be addressed for its efficient field operations (Fig. 12.1).

In a typical MES setup, the abiotic anodic chamber and the biotic cathodic chamber are separated by a proton exchange membrane (PEM) that allows protons to move from the anodic to the cathodic chamber (Fig. 12.2). At the anode, water molecules split into protons, electrons, and gaseous oxygen (Jadhav et al., 2022, 2024). As oxygen departs the anodic chamber, protons are carried to the cathodic chamber via the PEM, and electrons are dragged to the cathode via a potentiostat. The electron transfer from the electrode surface to

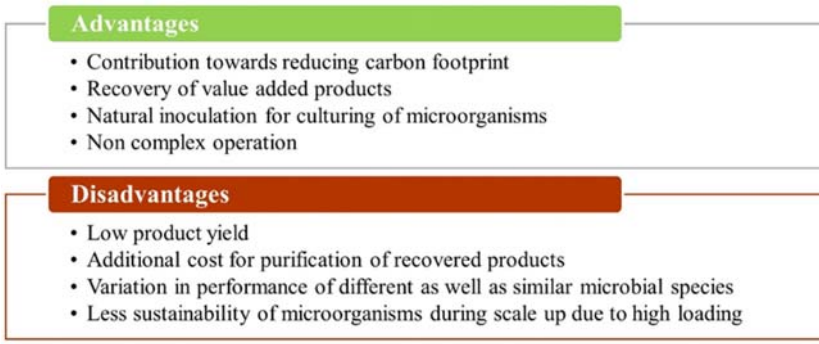

FIGURE 12.1 The advantages and disadvantages of microbial electrosynthesis.

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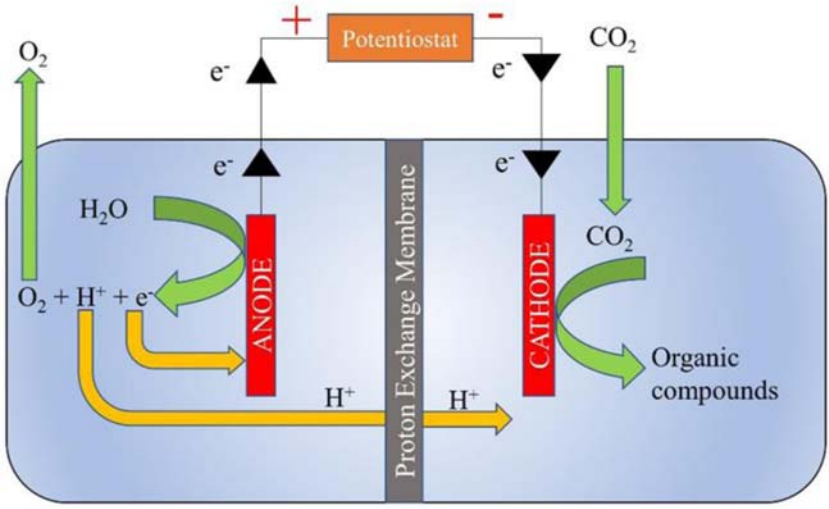

FIGURE 12.2 The working mechanism of microbial electrosynthesis and the reaction occurring therein.

the microbes generally occurs via direct electron transfer (DET) or indirect electron transfer (IET). The DET is the preferred mechanism in cases of continuous systems, where it contributes to preventing the loss of catalysts as well as the loss of electrons by maintaining direct surface contact between the biofilm and the cathode. However, biofilm formation on the electrodes restricts its electrochemical interaction, which subsequently reduces the product yield. On the other hand, IET is facilitated by electron shuttles/pili, which help in the transfer of electrons by transporting them from the electrolyte to the electrode surface. This IET mechanism can be improved by hydrogen or other capacitive particles (quinones, viologens etc.), which could also be synthesized within the MES system itself (derivatives of phenazine and flavin) (Das et al., 2020).

Biocatalysts then combine these electrons, protons, or energy carriers, such as hydrogen and CO_2, in the cathodic chamber to produce primarily volatile fatty acids. The electrode-driven chemical processes employed for carbon sequestration ensure sufficient electrocatalytic activity, but chemical catalysts are typically too costly to be scaled up for practical uses (Sapountzi et al., 2017). On the other hand, due to the superior adaptability of biocatalysts, which can be enzymes, an organelle, or even whole cells, has attracted attention in various innovative processes (Rasheed et al., 2023). Additionally, the cost of growing microbes as microbial catalysts is negligible/low, and the microbes catalyzing the processes obtain adequate energy for cell maintenance during the process itself; as a result, they are long-lived and self-sustaining (Wang et al., 2020). Therefore, the use of biocatalysts in MES makes the technology both cost-effective and environmentally benign. Although various changes in the

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design components and operational parameters, such as different electrode materials (Aryal et al., 2018; Das, Chakraborty, et al., 2021; Das, Das, et al., 2021), biocatalysts (Blanchet et al., 2015; Wang et al., 2021), mode of operation (batch and continuous) (Batlle-Vilanova et al., 2016; Das & Ghangrekar, 2021), etc. have been incorporated in numerous studies pertaining to MES; however, the basic working mechanism of the technology remains the same.

2. Biocatalyst employed in microbial electrosynthesis

One of the key elements influencing the performance of MES is the electrotrophic biocatalyst employed. Electrotrophic microbes that use electrons as the energy source sequester carbon dioxide to produce value-added organic chemicals in MES. Further in MES, both pure or mixed microbial consortia and even enzymes can function as biocatalysts. However, both pure and mixed culture inocula possess their own limitations and benefits (Fig. 12.3). Like, pure culture provides ease of parametric optimization; however, mixed cultures have better yields and growth rates because of their higher adaptability (Dessì et al., 2021). The autotrophic bacteria, including *Clostridium ljungdahlii, Clostridium aceticum, Moorella thermoacetica, Sporomusa ovata, Sporomusa sphaeroides,* and *Sporomusa silvacetica*, have been used for the successful demonstration of acetate production by electrode-driven CO_2 fixation in MES (Abdollahi et al., 2022). Apart from that, several other species such as *Trichococcus palustris* sp., *Oscillibacter* sp., *Clostridium propionicum*, *Clostridium celerecrescens*, *Desulfotomaculum* sp., *Tissierella* sp., etc.

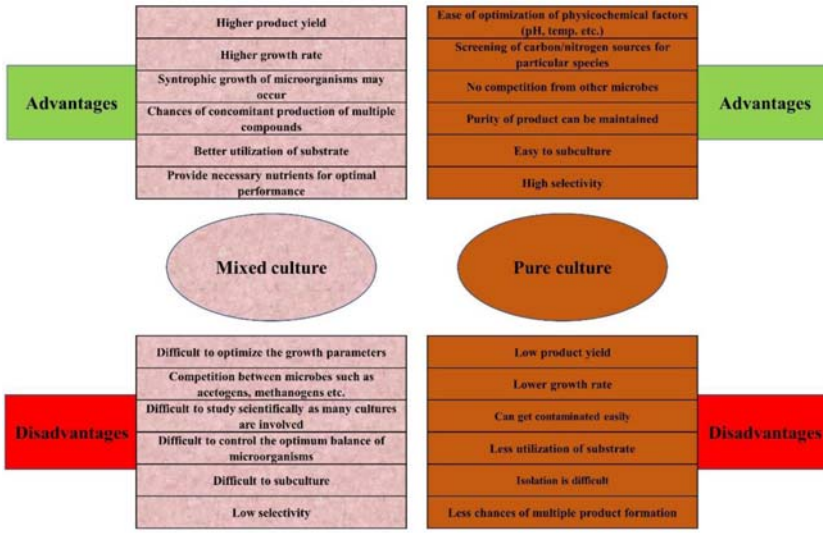

FIGURE 12.3 Advantages and disadvantages of using mixed and pure culture in MES.

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exhibited CO_2 reduction in the biocathode of MES (Das et al., 2019). Acetogenic bacteria, including *S. ovata, S. sphaeroides, Clostridium ljungdahlii,* and *Moorella thermoacetica*, have been proven to reduce CO_2 to acetate by accepting electrons from an MES cathode, in contrast to other microorganisms, like *Acetobacterium* sp., which use locally produced H_2 as the electron source. Bai et al. (2020) demonstrated the use of *Methanococcus maripaludis* that converted CO_2 and on-site electrochemically generated H_2 to methane via indirect H_2-mediated electromethanogenesis.

3. Products recovered via microbial electrosynthesis

A wide variety of products can be generated via MES, and as a result, researchers are employing it to produce both gaseous and liquid organic compounds from carbon sequestration. This unique ability of MES can be ascribed to the electrotrophic microbes residing in the cathodic chamber of MES, which possesses the ability to catalyze electrochemical processes, such as proton reduction to produce molecular hydrogen or the reduction of carbon dioxide to organic compounds such as methane, acetate, etc. (Rosenbaum & Henrich, 2014), thus offering great potential in the production of biofuels and other commodity chemicals. The various products reported to be produced by MES are explained in detail subsequently (Table 12.1).

Acetate is most frequently produced from CO_2 reduction in MES, which is generally used in pulp and paper industries as well as in pharmaceutical industries. Numerous other petrochemical products, including vinyl acetate monomer, terephthalic acid, and ethyl acetate, are produced using acetate as a raw material in various industries (Straathof & Bampouli, 2017). As a precursor, it is also used to create latex emulsion resins, adhesives, finishing agents for textile goods, cellulosic plastics, paper coatings, etc. Production of acetate by MES can be facilitated by either pure or mixed cultures of biocatalysts. *S. ovata*, which has been the mostly used pure culture for acetate production via MES, which has shown the highest production rates up to 47.3 ± 5.1 g/m^2.day as well as coulombic efficiency (CE) in the range of 80%−85% (Krige et al., 2021). However, most of the literature on MES is focused on mixed cultures as it has shown better results in terms of product recovery. For example, an augmented mixed culture dominated by *Acetobacterium* species produced more acetate than a pure culture of *C. ljungdahlii* in the presence of CO_2-rich brewery gas. The mixed culture (66 ± 5.7 g/m^2.day) almost doubled the acetate production rates in comparison with the pure culture (34.6 ± 1.1 g/m^2.day), and similar observations were also made for the electron recoveries. More than $84 \pm 13\%$ of the electrons in the mixed culture MES were recovered in acetate, as opposed to $42 \pm 14\%$ in the pure culture (Roy et al., 2021).

During the bioelectrochemical reduction of CO_2 to acetate, acetyl-CoA (coenzyme) is used, which has the potential to serve as a building block for

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TABLE 12.1 Product recovery with various biocatalysts and electrodes used in microbial electrosynthesis.

Biocatalyst	Electrode material	Imposed potential (vs. SHE)	Products recovered (Yield)	References
Clostridium ljungdahlii	Graphite felt and stainless steel assembly	−0.69	Acetate (7.51 g/m^2.day)	(Bajracharya et al., 2015)
Sporomusa ovata	Stainless steel plate	−0.66	Acetate (8.2 g/m^2.day)	(Blanchet et al., 2015)
S. ovata	Carbon cloth	−0.69	Acetate (15.16 ± 1.42 g/m^2.day)	(Aryal et al., 2018)
Mixed culture	Gas diffusion electrode	−0.8	Butanol (62 mg/L.day)	(Srikanth et al., 2018)
Mixed culture	Carbon felt with TiO_2	−0.90	Ethanol (168.89 mg/L.day)	(Das et al., 2020)
			Acetate (268.75 ± 18.75 g/m^2.day)	
Mixed culture	Carbon felt with Rh	−0.90	Acetate (132.50 ± 10.12 g/m^2.day)	(Das et al., 2020)
Clostridium ljungdahlii	Nickel-phosphide/carbon felt	−0.19	Acetate (17 g/m^2.day)	(Wang et al., 2021)
Mixed culture	Carbon felt	−0.8	Methane (103.2 ± 4.94 mM/day.m^2)	(Dykstra & Pavlostathis, 2021)
Mixed culture	Carbon paper and methyl viologen	−0.85	Acetate (197.5 g/m^2.day)	(Anwer et al., 2021)
Mixed culture	Graphite rod	−0.7	Methane (44 mM/m^2.day)	(Vasiliadou et al., 2022)

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a variety of valuable organic compounds and biofuels including ethanol, n-butanol, alcohols, or longer-chain fatty acids (Pu & Han, 2022). Similar to ethanol, butanol and propanol can also be derived from MES using mixed culture (Lovley & Nevin, 2013). However, the major drawback of using CO_2 as an electron acceptor in the bioelectrosynthesis process from CO_2 to alcohols is the requirement of high electron demand (Quraishi et al., 2021). For instance, even though the theoretical potentials for the reduction of butyrate to butanol ($E^0 = 0.37$ V vs. standard hydrogen electrode, SHE) and the reduction of CO_2 to butanol ($E^0 = 0.30$ V vs. SHE) are similar, the reduction of butyrate to butanol only needs four electrons, whereas the reduction of CO_2 to butanol requires 24 electrons, implying a sixfold higher current requirement. In addition, the process of converting CO_2 to butanol would likely entail a number of synthesis stages, each of which will result in a certain efficiency loss (Rabaey & Rozendal, 2010).

As an alternative to acetic acid, MES systems can also produce methane. Since the potential thermodynamic energy input of DET is smaller than that for IET mediated via H_2, Bai et al. (2020) sought to encourage a direct cell-to-cathode contact for the pure culture of *Methanosarcina barkeri*. A cage-type electrode was built for the DET, which made it easier for *M. barkeri* to adhere and enabled appropriate nutrition delivery. The findings demonstrated that when the potential was more negative than −0.6 V versus Ag/AgCl, direct electron transfer was the primary pathway for methanogenesis. However, as the potential was raised from −0.4 to −1.2 V versus Ag/AgCl, the production rates increased by 10 times, demonstrating that *M. barkeri* is more efficient at producing methane through a H_2-mediated electron transfer pathway than through DET. As of now, the maximum methane production rate of 12.5 L CH_4/L.day with a current-to-methane efficiency of 65% has been achieved by utilizing a mixed culture from a biogas plant. Although hydrogen was detected at a current density over 2.5 mA/cm^2, indicating that the biocatalyst may have metabolic constraints, the methane generation rate in this investigation was demonstrated to grow linearly with the applied current (in the range of 0.5−3.5 mA/cm^2) (Geppert et al., 2019). Methane has also been frequently observed as a coproduct in acetogenic MES (Aryal et al., 2020; Nelabhotla & Dinamarca, 2019). Methanogenic organisms may compete with acetogens for H_2 and even convert carboxylic acid into methane, when mixed cultures are employed as inoculum and MES cells are operated at neutral pH. Methanogenic development can be inhibited by pretreating the inoculum, such as with heat (Bajracharya, Yuliasni, et al., 2017) or chemical treatment (Marshall et al., 2013), albeit these methods do not guarantee complete methanogenesis suppression.

4. Product purification strategies

Although MES is capable of producing various industrial chemicals, the products derived are generally mixed with the broth because of the high

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solubility of short-chain organic acids and hence require additional downstream processing. This extraction can be done by conventional processes such as ion exchange resins, which provide the basis for adsorption (Reyhanitash et al., 2017), concentration/pressure-driven membrane processes (nanofiltration, forward osmosis, etc.) or electromembrane processes (electrodialysis, electro deionization, etc.). Another approach toward product extraction is the integration of membrane electrolysis, in which a stack of anion and cation exchange membranes is placed to provide an intermediate, middle recovery/extraction chamber between the anodic and the cathodic chamber. However, only limited literature is available on the usage of downstream processing techniques in the case of MES systems. Gildemyn et al. (2015) reported the acetic acid concentration of up to 13 g/L in the central extraction chamber via a stacked system, which separates the product through a single operational system, thus increasing the economic viability of the product recovered through MES. The modular approach in MES systems was further demonstrated by Das et al. (2021), in which acetic acid yield was 104.26 ± 1.75 g/m^2.day in the extraction chamber with CE and carbon recovery of $60.60 \pm 7.62\%$ and $3.08 \pm 0.35\%$, respectively. The separation of acetate from the catholyte after its production has also been demonstrated by Bajracharya, Van Den Berg, et al. (2017), in which anion exchange resin (Amberlite FPA53) was used to retain an acetate concentration of 10−20 mg/g of resin. In another experiment, 252.4 mM of butyrate was extracted by a hollow fiber membrane constructed of polypropylene (Batlle-Vilanova et al., 2017). The economic viability of these integrated separation processes demands that research focus should be concentrated on the modification of such techniques to make them scalable.

5. Scale-up attempts of MES

The technology of MES has the potential to produce industrial chemicals while maintaining economic viability and exemplifying sustainability. Although a lot of research is being carried out to improve the design components and potential of recovery of other high-valued products at the lab scale, there have only been limited successful attempts for scaling-up of MES. One such attempt showcased methane production with an upscaled two-chamber MES reactor having a volume of 50 L (Enzmann & Holtmann, 2019). This upscaled MES produced methane at a rate of 11.7 mM/day with a current density of 85 mA/m^2. This was the highest rate of methane generation documented for pure culture in the literature. However, the space−time yield, which is used as a foundation in scale-up investigations, was one-sixth than that of the lab-scale system. Another attempt was made by Ceballos-Escalera et al. (2020) in which a 32 L MES setup with 45 stacked reactors was fabricated. The system used a mixed culture of microorganisms derived from anaerobic sludge from a wastewater treatment plant and was able to produce

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methane at the rate of 4.4 L/m^2.day. Even after these demonstrations, there are certain bottlenecks for further scaling-up of MES systems to an industrial scale that needs addressing. Due to the uneven distribution of applied potential inside a large cathodic chamber/cathode, controlling the working electrode potential is not feasible for large-scale reactors. A large-scale system would also need a significantly higher volume of inoculum, which also adds to the cost incurred during transportation (Perry et al., 2020). Further, the yield of valuables recovered via scaled-up MES also needs to be enhanced considerably to take this technology from the lab to the field and further expedite the process of commercialization.

6. Technoeconomic and life cycle assessment

According to a comparison study between the economic viability of methanol carbonylation, direct ethane oxidation, anaerobic fermentation (AF) and MES, the molar yield of acetate produced by AF and MES must be significantly increased to compete with other well-established technologies. Due to the lower yield of MES and AF, production and investment costs were found to be considerably higher for these two technologies (Christodoulou & Velasquez-Orta, 2016). However, the amalgamation of these two technologies resulted in the production of acetate at a competitive price (0.24 £/kg), considering its present market value (0.48 £/kg) (Christodoulou et al., 2017). Among the products that can be derived from MES, acetic acid has the highest energy requirement (154,747 GJ), which can be related to the fact that thermodynamically, acetic acid (874.82 kJ/mol) requires more energy to synthesize than formic acid (269 kJ/mol) (Christodoulou et al., 2017; Savla et al., 2021). Alternatively, the energy required to produce formic acid was 8158 GJ, which is 13 times less than that required to produce acetic acid (Christodoulou et al., 2017; Savla et al., 2021). These results were partially influenced by the energy ratios and the number of electrons necessary to create the intended product. The electrochemical process used to produce acetic acid uses two times ($4e^-$) as much energy as formic acid synthesis ($2e^-$), resulting in a larger energy requirement.

When fossil fuels are used to create power, the contribution to global warming is strongly connected to energy requirements. Christodoulou et al. (2017) reported that the global warming potential of producing acetic acid (61,638 t CO_2 eq.) and propionic acid (48,797 t CO_2 eq.) was much higher than that of ethanol (−7526 t CO_2 eq.), methanol (−5577 t CO_2 eq.), and formic acid (−4428 t CO_2 eq.). In another recent study, after the evaluation of five different MES reactors for the production of different products, Tobechi et al. (2021) reported similar observations in which MES reactors exhibited a net positive global warming potential in the case of acetic acid (16,000 t CO_2 eq.) and propionic acid (22,100 t CO_2 eq.). However, in this case, even the production of ethanol (39,095 t CO_2 eq.) and methanol (30,200 t CO_2 eq.) also

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contributed significantly to the environmental emissions, which was attributed to the amount of energy required for their production (380,371 GJ for ethanol and 286,479 GJ for methanol). The only significant exception was formic acid, whose production resulted in negative global warming potential (−170.77 t CO_2 eq.). These results suggest that the researchers should also try to focus on imparting higher degree of environmental sustainability to this inventive technology of MES by reducing the environmental impacts arising from it.

7. Summary and future perspective

The inability of MES systems to scale, either by increasing size or by stacking configurations, and being subject to specific design and operational constraints, is the reason why their technological transformation is not yet a reality till date. It will take a lot of research to get a thorough grasp of the microbial dynamics in the scale-up reactors since our knowledge of the microbial activities taking place within an operational reactor is still in its infancy. If industrial flue gas is directly used as feedstock for MES, the extremely high temperature of the flue gas can adversely affect the survival of electrotrophic microbes. Moreover, the electrode material may suffer as a result of high temperatures and the presence of harmful chemicals in the flue gas. However, to overcome this, the system's gas pipes can be equipped with particular gas filters. On the other hand, the catholyte is a combination of different by-products that must be separated, thus increasing the cost of the manufacturing process. The downstream cost can be significantly decreased if the purity of the products generated can be reached by utilizing pure or genetically engineered microbial strains. Because the biocatalysts employed in the process of MES do not require high temperatures to function and are not harmful to the environment, the application of MES for the synthesis of acetate in this case is advantageous and environmentally friendly. The microbiome utilized in the procedure is self-sustaining; thus, replacing them on a regular basis is not necessary. As a result, MES can offer a different, efficient method for producing acetic acid from CO_2. Low product titer, which significantly raises the cost of acetate synthesis, is the main disadvantage of MES. Using multiple small, stacked reactors is one solution to this issue. However, it increases the capital expenditure required for the field-scale implementation of MES.

The embryonic technology of MES is still in its early stages; thus, the future investigation should focus on improving the product titer and rates at higher coulombic and energy efficiencies, thus accelerating the scaling-up of this technology. The capital investment for the setups might be significantly reduced by cost-effective reactor design and the use of inexpensive electrodes. CO_2 is the feedstock utilized for MES, and it is widely available in the atmosphere. However, intake gas must still be captured and purified, which again incurs a significant capital expenditure. To overcome this, industrial flue gases

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can be used as feedstock in MES. However, the flue gas emissions from various industries have a very diverse composition that includes particulate matter, and hazardous gases, including H_2S, NH_3, SO_x, and NO_x, in addition to CO_2. When these gases interact with water, they form acids or bases that can dramatically change the catholyte's pH and negatively impact the cathodic microorganisms' and the electrode material's activity. Hence, proper pretreatment of the flue gas is required prior to its application as feedstock in MES.

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Chapter 13

Application of the microbial carbon capture cells for CO_2 sequestration

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Abstract

Microbial carbon capture cells (MCCCs) are a type of microbial fuel cell (MFCs) that are an effective technology to remove nitrogenous and phosphorous compounds from the wastewater to generate bioelectricity and simultaneously produce algal biomass through CO_2 sequestration. The cultivated algal biomass is of high significance as the biomass can be extracted to effectively generate value-added by-products. By utilizing bacterioalgal symbiotic consortium, MCCCs efficiently perform CO_2 sequestration to reduce even point source carbon dioxide emission. Few advantages of MCCCs over other type of MFCs are that the oxygen released in the cathode compartment during the light phase of algal photosynthesis reduces the cost of external aeration, thereby decreasing the overall operation cost. Other than extracting value-added by-products from the harvested algal biomass, it can be used as a direct feedstock in the anodic chamber to be used as the substrate, and when used in the cathodic chamber, it can be used to produce bioethanol.

Keywords

Algal biomass; CO_2 sequestration; Exoelectrogenic bacteria; Microbial carbon capture cell; Microbial fuel cells; Wastewater treatment.

1. Introduction

Since industrial revolution began in the 1700s, there has been a constant increment in CO_2 emission. CO_2 emission in larger quantity leads to irreversible change in climatic conditions. The 21st century will also see a rise of 0.4−1.0 m in global sea level if carbon emission surpasses 600 ppm by

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volume. Present scenario of CO_2 emission is 385 ppmv (parts per million by volume) (Solomon et al., 2009). Thus, there is an urgent need of some advance technology that can effectively lead to CO_2 sequestration.

Technologies with traditional wastewater system have a high input for energy, and they also emit huge amount of CO_2 into the environment (Jadhav et al., 2022). In this aspect, microbial fuel cells (MFCs) are a new age technology that has the ability to recover electrical energy while breaking the organic pollutants in the wastewater making it a self-sustaining process (Aelterman et al., 2006; Nayak & Sevda, 2022; Prasad et al., 2020; Sevda & Abu-Reesh, 2018; Sevda & Sreekrishnan, 2014). But when glucose or acetate and even real wastewater is used as a substrate, then there is release of CO_2 (Freguia et al., 2007). Almost half of the organic carbon present in wastewater is the result of discharges from industries using fossil fuels. Now, if considered that the chemical oxygen demand (COD) of a certain wastewater is 1200 mg/L, and the major organic content is glucose (total carbon (TC)/COD = 0.5 w/w), and in the end there is a total conversion of all organic carbon into CO_2, then per 1200 t of wastewater treated, there will be ∼1,6OOO t of CO_2 released. In traditional conception of greenhouse gas management, respiration and metabolism of bacteria are not considered, but sequestration of these CO_2 can further decrease atmospheric CO_2 concentration. As the operational time of a dual-chamber MFC increases, cathodic pH also increases due to build-up of OH^- ions, which are released in oxygen reduction reaction (ORR) process (Gil et al., 2003; Rozendal et al., 2006), thereby creating an alkaline environment in the cathodic chamber, which can readily absorb CO_2 from the anode.

In recent years, great efforts have been put into development of new technologies that can efficiently recover renewable energy from wastewater (Jadhav et al., 2021), and one such technology is bioelectrochemical systems (BESs), because the energy that these systems can harness from the organic content of the wastewater are much more than that is required to treat the wastewater system (Cheng & Logan, 2007; Feng et al., 2010; Gattrell et al., 2018; Heidrich et al., 2011; Sevda et al., 2015; Sevda et al., 2016; Wang et al., 2013; Wang & Ren, 2013). However, the aforementioned technology can only reduce fossil fuel−related carbon utilization and discharge. So, currently active research is being conducted to enhance the working principle of BESs such that they can work as both energy source and carbon sink as a thorough CO_2 mitigation strategy (Gunaseelan et al., 2021; Patwardhan et al., 2021).

For curbing industrial CO_2 discharge, which roughly accounts for 60% of total CO_2 discharge due to fossil fuel consumption, point source mitigation strategies are applied. One such strategy is carbon capture and storage (CCS) (Samanta et al., 2012). However, there are few drawbacks of conventional CCS: apart from consuming huge amount of energy, they also become cost-intensive because of expensive CO_2 purification and separation step

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followed by compression, transportation, and storage. Apart from the aforementioned expenses, CCS adds as much as 10%–40% energy demand because of solvent/sorbent regeneration process (Yang et al., 2014). Membrane technologies such as BESs can greatly reduce the cost incurred by solvent/sorbent regeneration process, but scaling up these systems is a huge challenge (Espinal et al., 2013). To absorb more CO_2 from atmosphere, CCS technology has been used along with biomass combustion/energy production, BECCS (Biorecro, 2010), or using base solvent absorption (Holmes et al., 2004; Socolow et al., 2011; Stolaroff et al., 2008) or solid sorbent adsorption (Lackner, 2009; Choi, Lee, et al., 2011; Choi, Drese, et al., 2011). But these technologies are higher in energy demand and thereby much more expensive than point-source CO_2 mitigation (House et al., 2011). Recently, researches on BESs with algal culture in cathodic chamber to absorb and utilize CO_2 released from the anodic chamber in a microbial carbon capture cell (MCCC) have been extensively studied, and it has been proposed as a cheaper and much effective air CO_2 removal strategy (Wang et al., 2010). Other related researches have shown that acids that are released in the anolyte while electrolysis of saline water in microbial desalination cells (MDCs) can actively react with minerals such as carbonate or silicate to produce strong alkaline environment that readily absorbs CO_2 (Rau, 2008; Rau et al., 2013). In the aforementioned electrolysis process, water molecule splits to generate H_2 molecule whose market value can in turn neutralize the cost of the process, and if the bioelectricity generated from the system itself is used to run it, then it can become a complete CO_2 emission negative system (Sarma et al., 2021). This chapter provides concise knowledge on MCCC, its types, and working principle along with discussion of role of MCCC in CO_2 sequestration and algal biomass generation. Future prospectives and scopes of this technique are also discussed.

2. Microbial carbon capture cell

MFCs are a branch of BESs that are separated into anodic and cathodic chamber by proton exchange membranes (PEMs) (Jadhav et al., 2017, 2020). Both the chambers have electrodes, which are connected by an external circuit. Depending on the kind of catholyte used, MFCs can be classified into abiotic catholyte MFCs, which utilize substrates such as potassium ferricyanide, nutrient medium, etc. and biotic catholytes such as algae, cyanobacteria, etc (Patel et al., 2021). The latter category henceforth is referred to as MCCC. The technique used in MCCC puts together either autotrophic or phototrophic microorganisms such as algae in the cathode chamber as well as the exoelectrogenic bacteria in the anode chamber (Velasquez-Orta et al., 2009). Depending on the role of the algae in the MFC, it will be consumed as a substrate because it is a rich source of carbon or will produce oxygen inside the chamber; algae are thereby grown in either the anode or the cathode

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chamber of an MFC. In the cathodic compartment, algae can grow passively by consuming CO_2 directly from the environment (Melis & Melnicki, 2006) or when the chamber is sparged artificially with CO_2 gas (Cui et al., 2014). The necessary amount of light can be taken up from either direct sunlight or from lights set up artificially in the lab under precise conditions (Rashid et al., 2013). Substrate can be anything ranging from simple glucose, formate, or acetate to complex matters present in a variety of wastewater such as domestic, municipal, industrial wastewater, or even landfill and food-processing leachate (Li et al., 2013; Tugtas et al., 2011).

Currently, the usage of wastewater, which acts as a substrate in MCCC for production of power, is being heavily studied. Table 13.1 shows different MCCCs that have been studied with power output and COD removal efficiencies.

3. Working principle of microbial carbon capture cell

A standard MCCC is illustrated Fig. 13.1. The key principle behind the working protocol of MCCC is that the oxidative degradation of substrates in the anodic chamber utilizing anaerobic electrogenic microbes releases CO_2, electrons, and protons. These released CO_2, electrons, and protons can be concurrently used by photosynthetic microbes in the cathode compartment for sequestration of CO_2 as well as biomass and bioelectricity generation (Sivakumar et al., 2018). For the photosynthetic microorganism being used in the cathode compartment of the MCCCs, when a single-chambered MCCC is used, algae are grown as a biofilm attached to the air cathode. This air cathode is directly exposed to air. In double-chambered MCCC, when algae are introduced in the cathode compartment, instead of oxygen, these algae act as the terminal electron acceptor, thereby generating biomass. Algae through photosynthesis also increase dissolved oxygen content in the cathodic chamber, which in turn promotes electron reduction at the cathode (Gajda et al., 2013; Gajda Iwona, 2016; Ucar et al., 2017).

The biochemical reactions that proceed in an MCCC are as follows (Zhang et al., 2019).

3.1 Anodic chamber: oxidation

The microbes present in the anodic chamber hydrolyze and degrade the organic molecules $(CH_2O)_n$ to release CO_2, H^+, and electrons (Jadhav et al., 2017). The oxidation process may be carried out either electrogenic microbial community or by the algal community or by both when a bacterio-algal fuel cells is used (Li, Zhou, Luo, et al., 2019; Zhang et al., 2019).

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$

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TABLE 13.1 MCCCs studied with different substrates and their power output and COD removal efficiencies.

Serial no.	Content of cathodic compartment	Content of anodic compartment	(%) Removal of COD	Power output (mW/m^2)	References
1	*Chlorella vulgaris*	–	–	48 mA/m^2	Jeon et al. (2012)
2	*Scenedesmus obliquus*	Activated sludge	–	1.77 W/m^2	Rashid et al. (2013)
3	*Chlorella and blue green Phormidium*	Wastewater	82	264	Juang et al. (2012)
4	*C. vulgaris*	Activated sludge	80.5	13.6	González Del Campo et al. (2013)
5	*C. vulgaris*	Domestic wastewater	–	5.3 W/m^3	Wang et al. (2010)
6	Mix algal culture	Municipal wastewater	–	11.6	Lobato et al. (2013)
7	*C. vulgaris*	Enriched bacterial consortium	–	62.8	Gajda et al. (2015)
8	*Chlamydomonas reinhardtii*	*Geobacter sulfurreducens*	–	40	Nishio et al. (2013)
9	*C. reinhardtii*	*G. sulfurreducens* + acetate	–	631	Nishio et al. (2013)
10	*C. reinhardtii*	*G. sulfurreducens* + formate	–	139	Nishio et al. (2013)
11	*C. vulgaris*	*Scenedesmus*-enriched anaerobic-activated sludge	91	514	Richardson et al. (2012)
12	*Spirulina platensis*	–	–	10	Lin et al. (2013)
13	*S. obliquus*	GM media only	–	154	Kakarla and Min (2014)

Continued

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TABLE 13.1 MCCCs studied with different substrates and their power output and COD removal efficiencies.—cont'd

Serial no.	Content of cathodic compartment	Content of anodic compartment	(%) Removal of COD	Power output (mW/m^2)	References
14	Blue green algae	Anaerobic wastewater sludge	81	115	Yuan et al. (2011)
15	*Laminaria saccharina* liquor (autoclaved)	Wastewater microbial consortium	89	219	Gadhamshetty et al. (2013)
16	*Desmodesmus* sp.	Synthetic wastewater	–	98	(Wu et al., 2014)
17	*Synechococcus leopoliensis, Anabaena cylindrical, Chlorella pyrenoidosa*	*Shewanella oneidensis*	–	0.0034	Walter et al. (2013)

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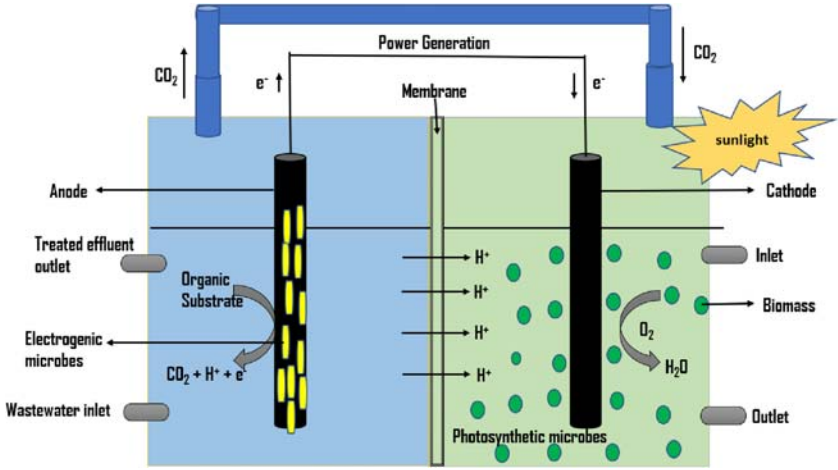

FIGURE 13.1 Working principle of a typical microbial carbon capture cell (MCCC).

3.2 CO_2 utilization and photosynthesis

In some MCCCs, where algae are utilized in both anodic and cathodic chambers, external supply of CO_2 may be required to boost photosynthesis and biomass generation of the organism via carbon fixation (Li, Zhou, Luo, et al., 2019). Therefore, the total CO_2 content of the system is the summation of the CO_2 that have been supplied externally along with the CO_2 liberated from the oxidation of organic matter. The liberated CO_2 is uptaken by algal cell wall and, in the presence of light, is utilized to generate matter, which is used for growth and maintenance of the algae cell, as well as by-product formation (Zhou et al., 2012).

$$nCO_2 + nH_2O \rightarrow (CH_2O)\ n + nO_2 \text{ (in the presence of light and algae)}$$

3.3 Cathodic chamber: reduction

In most of the researches done on MCCC, it is the cathodic chamber that is introduced with the algae (Bazdar et al., 2018; Bazdar et al., 2018; Li, Zhou, Tan, et al., 2019; Nguyen & Min, 2020). In the cathodic chamber in the presence of oxygen, the electrons transferred via the external circuit and the protons passing into the cathodic chambers through PEMs combine to generate water. Other than this, oxygen is also produced directly from photosynthesis by the algae.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

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4. Types of microbial carbon capture cell

There are mainly three types of MCCCs that are currently being used for simultaneous bacterial and algal growth: (1) single-chamber MCCCs, (2) double-chamber MCCCs and, (3) triple-chamber MCCCs. In single-chamber MCCCs, growth of bacteria and algae occurs in one single anodic chamber, and in the cathodic chamber, an air cathode is used, which is directly exposed to air (Chandra et al., 2012; Nishio et al., 2013; Yuan et al., 2011). Advantages of single-chamber MCCCs are that they are membrane-less, feasible to use and scale up, cost-effective, and easily manageable in lab scale when compared with other types of MCCCs. Single-chamber MCCCs can synergistically grow autotrophic bacterial and heterotrophic algal coculture with 98% consumption of the generated CO_2 (Nishio et al., 2013).

In double-chambered MCCCs, algae and bacteria are grown in two chambers separated by CEM (Gadhamshetty et al., 2013; Rashid et al., 2013). The cathodic side of the chamber has the algal growth and is commonly illuminated by light, which provides the photons required for algal photosynthesis. But this illumination also affects the anodic chamber that has bacterial culture; therefore, the anodic chamber needs to be covered up during the run time of the MCCC (Juang et al., 2012). In few researches, for continuous source of algal culture and to avoid illumination of both anodic and cathodic chamber of the MCCCs, an external algal photobioreactor that is connected externally to the cathodic chamber has been studied (Gajda et al., 2013; Juang et al., 2012). Although in double-chambered MCCCs maintenance of continuous supply of algal culture is easy, one of the major disadvantages in an H-shaped double-chambered MCCCs is small area of CEM that is available for ion exchange, leading to low power output. Also, if additional pumping of air is done in the cathodic chamber, it further reduces the net power production. Fouling of PEM and high internal resistance are other disadvantages of double-chambered MCCCs.

In triple-chambered MCCCs, an extra chamber is maintained in between the cathodic and anodic chamber. This type of MCCCs is useful in desalination of water, as cations approach the cathode and anions approach the anode, desalination occurs in the middle chamber. Studies have shown that when salt water is treated in the middle chamber of MCCCs, it reduces overall power production of the MCCC. The peak power density of the anodic and cathodic chamber is found to be greater than the middle chamber (Kokabian & Gude, 2013; Saba & Christy, 2015).

Some of the other types of MCCCs are tube-shaped MCCCs, which is a type of single-chambered MCCC and is usually lab scale (Yuan et al., 2011) and algal pond or algal lagoon, which have the anodic compartment dipped inside a pond containing algal culture or even larger algal lagoon. In any type of MCCCs, optimization of power production as well as biomass generation can be done according to local weather circumstances.

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5. Carbon sequestration using microbial carbon capture cells

Prokaryotes play different roles in CO_2 capture, utilization, and sequestration (CCUS) processes (Hicks et al., 2017). CCUS is a fast-growing methodology that attenuates anthropogenic CO_2 generation and its effect on the environment by capturing it from the point source of huge emitters and storage of the captured CO_2 in reservoirs for sequestration (Gislason et al., 2016). Conventional CCUS methodology had been altered to focus on the usage of microorganisms for their capability to assimilate carbon as well as to adapt to any environmental stress be it biotic or abiotic (Noble et al., 2012; Zhao & Su, 2014). Prokaryotic microbes adapt to the environmental stresses by alteration of their metabolic pathways by altered gene regulations, natural selection of beneficial genes, and their variants from within a population. Closely (Rudi et al., 1998) or even distantly related (Koonin et al., 2001), microbial population can undergo horizontal gene transfer to pass on the selected beneficial genes generation after generations (Stüken et al., 2011).

The most preferred microorganism for carbon sequestration is the eukaryotic alga. These microorganisms have high diversity and range from unicellular to multicellular, present in the form of either micro- or macroalgae (Chen et al., 2009; Wong, 2014). MCCCs with different algal cultures and their power output have been compared in Table 13.1.

Algae are photosynthetic organism that uses CO_2 through Calvin–Benson–Bassham (CBB) cycle. By using CBB cycle principal enzyme, the algae covert inorganic carbon to organic carbon compounds (Shi & Theg, 2013). This principal enzyme RuBisCo (ribulose 1,5-bisphosphate carboxylase/oxygenase) catalyzes carboxylation reaction of ribulose 1,5-bisphosphate, generating 2 moles of 3-phosphoglycerate (3PG) (Parry et al., 2003). One of the 2 moles of 3PG that was generated get consumed in the process of central metabolism while the other mole is used for cycle regeneration. However, RuBisCo has affinity for both CO_2 and O_2, and because the latter is available in much more amount in the environment, the oxygenase activity of RuBisCo gets activated and photorespiration starts to occur leading to formation of undesirable by-products (Parry et al., 2003). But with evolution, algae have developed their CO_2 sequestration pathway also known as carbon dioxide concentration mechanisms (CCMs) for maintaining balance between low level of CO_2 and increased demand of inorganic carbon (Meyer & Griffiths, 2013). Advantages of utilizing algae for CO_2 sequestration are that they have several different routes of growth such as autotrophic, mixotrophic, or heterotrophic depending on the requirement of their nutrition as presented in Fig. 13.2 (Zhao & Su, 2014). They uptake CO_2 much faster than any other microorganism and also generate easily extractable value-added by-products such as fertilizers and proteins (Arun et al., 2020; Cole et al., 2014; Mayfield et al., 2007; Zhao & Su, 2014). Few of the limitations of using algae in

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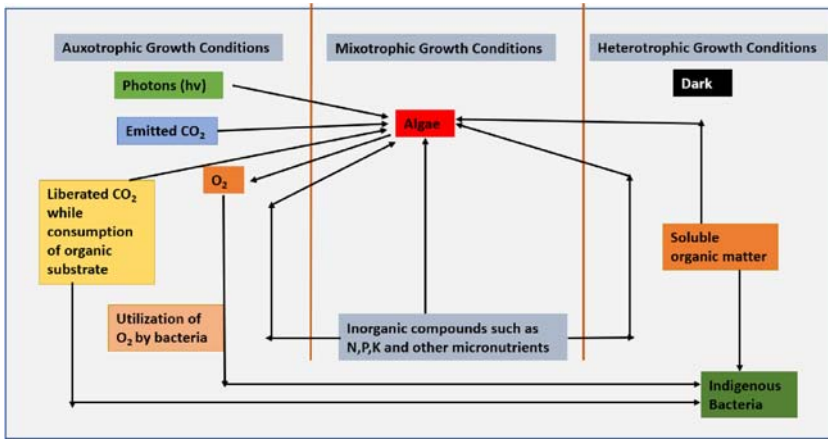

FIGURE 13.2 Different routes of algal growth such as autotrophic, mixotrophic, or heterotrophic.

MCCCs are their requirement of moist environs and high concentration of phosphorus as well as illumination of the chamber with light of optimum wavelength and intensity. Irrespective of their elementary structure and genetic make, cyanobacteria are much more efficient carbon fixer (Oliver et al., 2014), but they have very low biomass yield (Machado & Atsumi, 2012). Owing to their elementary genetic structure, modification of their genes for higher biomass generation is easy, like genetically modified RuBisCo with increased affinity (Rosgaard et al., 2012) for CO_2 or generation of higher amount of value-added by-products (Machado & Atsumi, 2012; Oliver et al., 2014). Due to very basic nutrient media requirement for cyanobacterial growth, cultivation of cyanobacteria is inexpensive, but cost-intensive part is agitation of the system during growth of cyanobacteria. Apart from these, any disturbances in temperature range (20−30°C), pH (7−9), or wavelength of the light affect the productivity and efficiency of the cyanobacterial culture. In generation of biomass, carbon and nitrogen content are the limiting factors (Wong, 2014). While much studies have been done using microalgae in both the chambers of MCCCs targeting treatment of wastewater as well as bioelectricity generation, very few studies are reported to have worked on enhancement of photosynthetic reaction utilizing external source of CO_2 in the cathode compartment of the MCCCs (Yadav et al., 2020).

Because MCCCs capture in situ CO_2, they lead to better sequestration of CO_2 emitted from the anodic chamber along with higher voltage generation (611 ± 51 mV) when compared with MCCCs that operate without external aeration because these MCCCs utilize the CO_2 from the anodic chamber. They can also use CO_2 directly from atmosphere, from gases released by ignition of fossil fuels or from fermentation industries, thereby reducing the cost needed to externally supply CO_2 (Chi et al., 2011; Wang et al., 2010). Researches have

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shown dissolved oxygen (DO) level in some of the cathodic chamber of MCCCs can reach up to 7.5 mg/L (saturation level of DO is around 7.5 mg/L). A voltage of 620 ± 40 mV is reported to be generated through MCCC when external aeration is supplied, and this value is comparable with voltage of 609 ± 40 mV generated through MCCC without supply of external aeration (Wang et al., 2010), showing that algal MCCC is effective in decreasing the cost of external aeration while generating the same amount of voltage.

6. Biomass generation using microbial carbon capture cell

Other than to treat wastewater and generate bioelectricity, algal MCCCs can be utilized to grow algal biomass in the cathodic chamber. Algal biomass is a rich source of carbohydrates, proteins, and lipid, which makes them an excellent candidate for antibiotic and biofuel such as biodiesel, bioethanol, biobutanol, and biohydrogen production. They can also be used as animal feedstock and generation of other by-products such as pigments, polyunsaturated fatty acids, and even antioxidants (Akubude et al., 2019; Das et al., 2020). Research with *Dunaliella salina* has shown that the biomass of *D. salina* contains photosynthetic pigment β-carotene. This pigment is extractable and can be used as a supplement for vitamin C and even as natural food coloring agent (Becker & Richmond, 2004; Pulz & Gross, 2004). Polysaccharides such as laminarin, fucoidan, and alginates have been shown to be extracted from brown algae such as *Fucus vesiculosus* and *Turbinaria conoides* biomass. These polysaccharide compounds contain high amount of antioxidants, which are utilized to produce antiaging cream (Je et al., 2009). Other high-value products have been extracted from species of algae such as *Botryococcus* sp., *Chlorella* sp., *Dunaliella* sp., *Haematococcus* sp., *Phaeodactylum* sp., *Porphyridium* sp., and *Spirulina* sp., which are being utilized to produce superfood as well as their by-products being used in cosmetic industries (Borowitzka, 2013; Rosenberg et al., 2008). In a study, Powell & Hill (2009) have produced bioethanol and concomitantly generated bioelectricity from biomass of beer yeast by using it as a substrate in the anodic compartment of MCCC, while treatment of wastewater and concurrent generation of biohydrogen from biomass of algal species such as *Scenedesmus obliquus* and *Chlamydomonas reinhardtii* in the cathode compartment of MCCC is thoroughly recorded in literature (Kosourov et al., 2002).

Biomass concentration inside MCCC chambers affects the light usage capacity of the algae, which in turn affects oxygen generation and power production efficiency inside an algal MCCC. To illustrate, Bazdar et al. (2018) have elevated biomass concentration in the cathodic chamber of MCCC from 3.50 to 3.99 g/L and the light intensity from 4999 lux to 99,999 lux to show that there is a decrement of 53.6% in coulombic efficiency (CE). The reason of decrement in the CE is that when concentration of biomass reaches saturation, all the photons applied to the MCCC get consumed in photosynthesis,

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thereby increasing the concentration of DO to the highest, leading to poor current generation and low CE. Apart from this, photoinhibition begins to start around 10,000 lux (Bazdar et al., 2018; Cheng et al., 2006; Logan et al., 2015). Mainly, the more the intensity of photon, the higher the biomass concentration till it reaches saturation and using most appropriate dark and light regime with optimum photon intensity leads to higher biomass generation and maximum power production (125 mW/m^3 at 24/00 light/dark regime) (Bazdar et al., 2018).

7. Future prospects

Although few studies have been done on filamentous algae by researches such as Ge et al. (2018), Marella et al. (2019), Neveux et al. (2016), and Vucko et al. (2017), still future research in this field is required as filamentous algae have an edge over macroalgae in terms of nutrient uptake, treatment of wastewater as well as biomass generation. Owing to several advantages of filamentous algae (Liu et al., 2020), reactors should be uniquely designed to offer larger areal space for growth of these types of algae.

Recently, Walter et al. (2020) have studied stacked MFC by attaching four MFCs in series and successfully checked the current generated by this system by powering the screen of a microcomputer (Nintendo GameBoy Color). This kind of stacked setup can be replicated to study CO_2 sequestration, wastewater treatment, and power production using algal MCCCs at pilot scale. Molecular biology and genetic engineering approach to modify certain algal genes for better CO_2 sequestration, biomass generation, uptake of heavy metals from wastewater, or even production of value-added products can be explored.

Effect of several parameters such as substrate, catholyte, anolyte, light intensity, pH, and temperature on power production as well as scale-up of MCCCs should be further studied. Mathematical modeling and life cycle assessment of reactors will help to design most effective setup for algal growth, which in turn will help to tackle the economic and performance-based scale-up of the MCCC systems. Research on outdoor MCCCs in presence of natural sunlight should also be heavily studied as this type of MCCC is not explored much.

8. Conclusion

As MCCCs have proven to simultaneously treat wastewater to generate bioelectricity and also produce algal biomass, the operational cost gets counterpoised by the economic benefits of the system. Till date, studies in this research area majorly focus on examining different algal species grown separately in anodic or cathodic chamber, but in current time, more detailed researches on symbiotic working mechanism between different bacterioalgal

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cultures are required. Practical implementation of this technology such as scaling up from lab to pilot scale and storage of the generated bioelectricity in capacitors needs to be explored. Establishment of optimum reactor design for maximum power output and concurrent biomass harvesting is required.

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Chapter 14

Role of electrochemistry and electrochemical technologies for environmental bioremediation

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Abstract

Electrochemical technologies use electric current to break down toxic organic and inorganic compounds into simpler, less toxic compounds. These technologies are versatile, energy-efficient, and environmentally compatible and have been used for the remediation of various types of pollutants from the environment. Their utilization in organic and inorganic pollutants removal and heavy metals recovery by using micro-organisms to catalyze redox reactions on the electrodes has been extended in practice. Currently, electrochemical-based bioreactors are used to treat contaminated water, soil, or air pollutants, and even they can be designed to treat pesticides and degrade persistent organic pollutants. The significant challenges in electrochemical technologies are energy consumption and operating cost. However, using renewable energy-driven electrochemical device applications can mitigate these challenges.

Keywords

Bioelectrochemical systems; Bioelectrochemistry; Bioremediation; Electrochemical processes; Electrochemical technologies; Scaling-up; Wastewater treatment.

a. Equal contribution.

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1. Introduction

Electrochemical oxidation is a process that uses an electric current to break down organic compounds into simpler, less toxic compounds. This process can be used to treat contaminated water, soil, or air and can be coupled with biological treatment to enhance biodegradation. Electrochemical oxidation can also be used to generate reactive species such as hydroxyl radicals, which can help degrade persistent organic pollutants (POPs) that are resistant to biodegradation. Electrochemical reduction is a process that uses an electric current to convert toxic compounds into less harmful or nontoxic compounds. This process can be used to treat contaminated water or soil and can be coupled with bioremediation to enhance the removal of toxic compounds. The electrochemical reduction can also be used to convert toxic metals such as chromium or mercury into less toxic forms, which can be more easily removed from the environment. Electrochemical bioreactors are devices that combine the principles of electrochemistry and bioremediation to remove pollutants from the environment. These reactors use microorganisms to break down pollutants and electrochemistry to provide the energy required for biodegradation. Electrochemical bioreactors can be used to treat contaminated water, soil, or air and can be designed to target specific pollutants such as heavy metals, pesticides, or POPs. Electrokinetics is a process that uses an electric field to enhance the movement of contaminants through soil or water. This process can be used to mobilize and remove pollutants from contaminated sites and can be coupled with bioremediation to enhance the removal of contaminants. Electrokinetics can also be used to enhance the transport of nutrients or electron acceptors to microorganisms in the soil, which can improve the efficiency of biodegradation.

2. Electrochemical technologies

Population pressure, industrialization, agricultural expansion, urbanization, climate change, and other environmental crisis demand sustainable green technologies for environmental management (Oturan et al., 2011; Shah et al., 2019b; Venkatramanan et al., 2021). In addition, technological advancement and increased demand for consumer goods and services have caused environmental contamination (Oturan et al., 2011). Conventionally, environmental remediation involves the application of physical, chemical, and biological methods (Alkhadra et al., 2022). In the recent past, electrochemical methods emerged as a sustainable and innovative technology for environmental remediation and removal of toxic and refractory pollutants such as hazardous wastes, POPs, pesticides, heavy metals, and metalloids (Lacasa et al., 2019; Martínez-Huitle et al., 2023). Extensive application of electrochemical technologies in environmental bioremediation is due to its versatility, sustainability, pollutant removal capabilities, ease of handling, cost efficiency, and energy generation capabilities (Alkhadra et al., 2022; Chaplin, 2019).

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Electrochemical technologies are based on the principles of electrochemistry. Electrochemistry deals with the interaction between chemical reactions and electricity. Electrochemistry is concerned with the study of a chemical system involving electron transfer, properties of electrodes, and electrolyte behavior (Mukherjee et al., 2021). Electrochemical technologies have been applied for wastewater remediation since the 1960s, and their applications have widened to include environmental clean-up, energy conversion and storage, corrosion protection, and removal and recovery of metals (Quraishi et al., 2021). The reactions that take place in the electrochemical technologies such as oxidation, reduction, phase separation, and biological reactions provide opportunities such as scalability, treatment of diluted and concentrated effluents, and cost-effectiveness. Electrochemical technologies suitable for organic remediation, wastewater treatment, and toxic metal removal are electrocoagulation, electrooxidation, electro-Fenton's oxidation, electroflotation, electrodeposition, and electrobiological oxidation (Martínez-Huitle et al., 2023).

2.1 Electrochemical oxidation

It is most popular among the electrochemical advanced oxidation processes to degrade organic pollutants. It is widely used to treat textile wastewater as this process helps to remove the color of the wastewater (Rodríguez-Narváez et al., 2021). However, partial degradation of dye molecules results in products such as aromatic amines and other organic compounds. An electrochemical oxidation reaction involves the loss of one or more electrons from an atom/molecule at the anode surface when the electric current passes through the electrochemical cell (Alkhadra et al., 2022). It involves two mechanisms, namely, direct anodic oxidation and indirect anodic oxidation. Direct anodic oxidation (catalytic electrode oxidation) occurs at the interface between the electrode and electrolyte (Ha et al., 2024). The pollutants after adsorbing onto the anode surface are directly degraded. The direct oxidation process, however, often results in the fouling of electrodes and subsequent underperformance of electrochemical cells (Feng et al., 2016; Oturan et al., 2011).

In contrast, indirect anodic oxidation involves the generation of surface-active oxidizing species, which degrade the organic pollutants. The indirect anodic oxidation does not require an "oxidation catalyst" and also does not create oxidation by-products (Feng et al., 2016). The indirect electrochemical oxidation process also involves the production of ozone, hydrogen peroxide, and persulphate. The organic pollutants can also be oxidized/degraded using "electrogenerated active chlorine" (Yasri & Gunasekaran, 2017; Rodríguez-Narváez et al., 2021). The electrochemical oxidation process involves forming hydroxyl radicals, adsorbing hydroxyl radicals at the anode surface, and reacting hydroxyl radicals with organic pollutants.

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The anode material includes metal oxide, metal nanoparticles, carbon nanotubes, graphene, and graphene oxide (Yasri & Gunasekaran, 2017). The anode configuration, composition of anode material, and operation conditions influence the functioning of the electrochemical oxidation process, "current efficiency," "abatement effectiveness," and treatment methods (Alkhadra et al., 2022; Martínez-Huitle et al., 2023). Therefore, studies have focused on (1) the functional properties of different anode materials and (2) the efficiency of the electrochemical oxidation process in degrading different organic pollutants (phenolic compounds, aliphatic acids, etc.) (Martínez-Huitle et al., 2023).

2.2 Electro-Fenton's oxidation

Advanced oxidation processes involve the generation of highly reactive free radicals that can degrade organic pollutants. Electro-Fenton's oxidation process is one of the advanced oxidation processes (Oturan et al., 2011). Fenton's oxidation process involves the reaction of H_2O_2 and Fe^{2+} to form highly reactive hydroxyl radicals, hydroxide anions, and ferric ions. The Fe^{2+} catalyzes the reaction. The reactive hydroxyl radical reacts with organic molecules to release highly reactive organic radicals. The organic radicals react with H_2O_2 to release reactive hydroxyl ($OH^{\cdot}$) and alkyl peroxyl ($ROO^{\cdot}$). Fenton's reaction, as given by Yasri and Gunasekaran (2017) and Rashid et al. (2021), is as follows:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot}$$

$$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot}$$

$$R^{\cdot} + Fe^{3+} \rightarrow R^+ + Fe^{2+}$$

$$R^{\cdot} + Fe^{2+} \rightarrow R^- + Fe^{3+}$$

$$2R^{\cdot} \rightarrow R - R$$

The application of electric current in electro-Fenton's oxidation process is advantageous due to (1) regeneration of Fe^{2+} from Fe^{3+} at the cathode, (2) increased generation of reactive hydroxyl, (3) increased efficiency of degradation of pollutants, and (4) less sludge production. Based on the procedure of adding Fenton's reagent into the electrochemical cell reactor, the electro-Fenton's process is classified into three types (Yasri & Gunasekaran, 2017): (1) the Fe^{2+} is added externally and H_2O_2 is generated internally within the reactor. The H_2O_2 is produced in situ from the electrolysis process. The in situ production of H_2O_2 makes the process less risky to handle chemicals and also less costly. (2) In the case of the Fere-Fenton method, the reagents H_2O_2 and Fe^{2+} are added externally. (3) In the third case, both the reagents H_2O_2 and

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Fe^{2+} are generated within the reactor. The electro-Fenton's oxidation process has many advantages, as stated before. However, the pH of the electrolyte is a very important parameter for this process. A pH value of 3 is considered optimum for the efficient functioning of the process (Feng et al., 2016).

2.3 Electrochemical reduction

Electrochemical reduction is a chemical process by which an atom or a molecule gains an electron at the cathode under the influence of an electric current (Pandit et al., 2023). The electrochemical reduction process is used to treat effluents containing heavy metals, halogenated organic compounds, and inorganic anions, and the resultant product is relatively less toxic. This process is influenced by factors such as water quality, catalyst loading, and the potential of the cathode itself. The characteristics of the wastewater (low pH, devoid of competing ions, higher ionic strength) influence the performance of the electrochemical reduction process. The electrode configuration is also a significant factor influencing the performance. The electrode materials are made of silver, carbon, noble metals, etc. The advantage of this process is that besides treating pollutants, the pollutants are transformed into value-added products (Alkhadra et al., 2022).

2.4 Electrodeposition

The electrodeposition process involves the electrical deposition of metal ions in a solution on an electrode (cathode). This process is used to remove and recover metals from wastewater. For example, it is widely used to treat arsenic and copper wastes (Alkhadra et al., 2022). In addition, it has been used to recover gold-rich alloys using "vitreous carbon" and titanium flat cathodes in the "filter-press type electrochemical flow reactor" (Feng et al., 2016). However, electrodeposition efficiency is less due to the low mass transfer in the dilute effluent stream with less than 1000 ppm concentration. To increase the efficiency of the deposition of metals using the electrodeposition process, the thickness of the diffusion layer is reduced either through agitation of solution or increasing the concentration of the metals near the electrode surface. Further, the concentrator electrochemical technique, which involves placing the concentrator medium close to the cathode, is adopted to increase the concentration of metals near the cathode surface and increase the deposition of metals on the cathode (Yasri & Gunasekaran, 2017).

2.5 Electrocoagulation

The electrocoagulation process is based on the principles of electrochemistry and the agglomeration process. The agglomeration process involves coagulation and flocculation. While coagulation reduces the electrostatic force

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between the colloidal particles, flocculation enables the binding of colloidal particles to form floc. The electric current applied in electrocoagulation reduces the electrostatic repulsion and agglomerates the suspended solids/organic substances (Barrera-Díaz et al., 2018). The electrocoagulation process involves (1) electrochemical dissociation of iron or aluminum anodes into the electrolyte solution in the form of iron or aluminum hydroxides and (2) in situ coagulation and flocculation of iron or aluminum with the pollutants/suspended solids (Barrera-Díaz et al., 2018; Mollah et al., 2004). The iron or aluminum anode is used as they function on a broader pH range of 4−11 and are cost-effective. The metal hydroxides function as a flocculating agent. The agglomeration process can be enhanced using synthetic polyelectrolytes (starch, cellulose derivatives), polysaccharide gums, and synthetic polymers. Electrocoagulation process efficiency is influenced by the operating conditions, particularly the influent pH and applied current density. Optimum pH and a current density of 20−25 A/m^2 are preferred (Chen, 2004; Feng et al., 2016).

Electrocoagulation technology is used to treat effluents containing suspended particles, colloidal particles, and heavy metals. They are used to treat effluents from domestic wastewater plants, oily wastewater, food processing industries, pulp and paper mill industries, and dye and textile industries (Feng et al., 2016). Electrocoagulation technology is preferred as it is cost-effective and consumes less energy. In addition, the organic matter removal performance of the electrocoagulation process can be significantly improved when it is integrated with biological processes and other advanced processes (Alkhadra et al., 2022). Nevertheless, the nonselective removal of pollutants, regular replacement of iron or aluminum anode, massive amount of sludge deposition, "electrode passivation," and inconsistent coagulant production are the limitations of this technology (Yasri & Gunasekaran, 2017; Alkhadra et al., 2022).

2.6 Electroflotation

Electroflotation involves separating pollutants that float on the surface due to the bubbles of hydrogen and oxygen generated by water electrolysis. The electroflotation process is driven by water electrolysis at both electrodes, releasing oxygen (at the anode) and hydrogen (at the cathode). It is applied in conjunction with other processes such as electrocoagulation. Electrocoagulation and electroflotation processes are used to remediate effluents containing organic pollutants and heavy metals. It also removes oil and suspended particles in groundwater and mining wastewater. However, a massive amount of sludge generated through these processes requires further treatment. The advantages of this process are that valuable substances can be recovered from the wastewater without the use of chemicals and at relatively low energy consumption (Alkhadra et al., 2022).

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2.7 Electrodialysis

The electrodialysis process employs membrane technology for the separation of metal ions. The electrodialysis process involves using cation, anion exchange membranes, and electric current to separate the ions. Initially, this technology was used for the desalination of brackish water. The electrodialysis procedure involves passing the feed through the nonporous exchange membrane (arranged parallel to each other) and applying electric current perpendicular to the stacks of the exchange membrane (Alkhadra et al., 2022). In this method, certain complexing agents/chemicals (e.g., EDTA) are added to form complexes of one group of elements, and the complexes are disallowed to pass through the cathode exchange compartment. The performance of electrodialysis is dependent on (1) the number, properties, and configuration/arrangement of exchange membranes, (2) electrode properties, (3) types and composition of substrates, and (4) operating conditions (Alkhadra et al., 2022).

3. Bioelectrochemical technologies

Wastewater treatment and simultaneous energy generation from waste through bioelectrochemical technologies are sustainable environment management practices (Guo et al., 2020). Bioelectrochemical technologies use microbes to convert organic compounds (chemical energy) into simpler compounds and electrical energy (electrons). The energy-rich electrons are used either for electricity generation (microbial fuel cells [MFCs]) or for the production of hydrogen gas (microbial electrolysis cell) (Yasri et al., 2019). In addition, bioelectrochemical systems (BESs) or technologies have been applied for methane production, pollutant load reduction, and desalination (Wang et al., 2020).

The MFCs are made of an anode and cathode compartments separated by a proton exchange membrane (Jadhav et al., 2024). In the anodic compartment, the biocatalysts such as *Geobacter sulfurreducens*, *Saccharomyces cerevisiae*, *Rhodopseudomonas palustris, and Shewanella species* degrade the organic matter to release oxidation products, electrons and protons (Sharma & Kundu, 2010). The anodic respiring bacteria grow on the anode to form a biofilm. The electrons are transferred to the anode either through mediators or exoelectrogens. Exoelectrogens are a group of microorganisms that directly transfer electrons to the anode without the mediators. The electron transfer pathways include direct electron transfer through c-type cytochromes, "electron shuttle molecules" (riboflavin), or through specialized organs like pili (Santoro et al., 2017; Shah et al., 2019a; Venkatramanan et al., 2021).

The electron from the anode reaches the cathode through an electric load. The terminal electron acceptor in the cathode accepts the electron to form a hydroxyl ion. (OH^-). The proton from the anode chamber moves through the proton exchange membrane to the cathode chamber. The exchange membrane

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is used in the MFCs to (1) separate the anaerobic anodic chamber and cathode compartment, (2) minimize the loss of hydrogen, and (3) prevent the mixing of carbon dioxide (in the anode chamber) (Venkatramanan et al., 2021). In a half-biological cell, the anode compartment has "electrochemically active microorganisms" and the cathode compartment lacks microbial activity. However, the use of biocathodes enables the efficient application of biocatalysts/bacteria in the cathode chamber. The biocathodes are classified into two types, namely, aerobic biocathode and anaerobic biocathode. The aerobic biocathodes oxidize the transition metals (Mn^{2+}, Fe^{2+}) using microorganisms and oxygen, while anaerobic biocathodes use iron, nitrate, manganese, etc., as electron acceptors (Sharma & Kundu, 2010; Venkatramanan et al., 2021).

The electricity generation of MFCs is influenced by the composition and properties of the electrodes, the type of substrates, the activity of exoelectrogens/microbial community, and microbial cell immobilization (Santoro et al., 2017; Verma et al., 2021). The anode electrode is preferably made of conductive carbonaceous materials, carbonaceous fabrics, carbon nanotubes, and carbon plates (Santoro et al., 2017). The anode with large porosity, large surface area, and conductivity potential is preferred. Further, the type of anode material also influences the immobilization of anodic respiring bacteria. As regards the substrate, which is the feed source for the anodic bacteria, several studies have been reported on the types of substrates, performance, and potential of different substrates. The use of complex substrates enriches the microbial community.

The applications of MFCs include wastewater treatment and removal of organic compounds, nitrogen, phosphorus, sulfide, and heavy metals (Guo et al., 2020; Shah et al., 2019a; Venkatramanan et al., 2021). The challenges to MFC applications include low power output, low removal rates of pollutants, electrode deterioration (fouling, corrosion, clogging), the activity of anode-respiring bacteria, and high initial and maintenance costs (Venkatramanan et al., 2021). Fouling is a process of accumulation of foulants such as organic compounds, "mineral scales," and colloids on the solid surface of the electrochemical cell reactor. The salts present in the solution, such as sulfate, calcium, magnesium, and bicarbonate, precipitate on the solid surface. Fouling reduces the performance of the electrochemical process, as they increase the electrical resistance and also the operating cost. Fouling can be managed by adopting physical and chemical treatment methods and the application of polyelectrolytes (Alkhadra et al., 2022).

4. Bioelectrochemical approaches for organic remediation

There are majorly two types of BESs: MFCs and microbial electrolysis cells (MECs). While MFCs are mainly used for bioelectricity production, MECs are used to produce biohydrogen, biomethane, and other value-added products (Patil et al., 2015). When microorganisms are added to the anodic chamber, it

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is referred to as bioanode, and when added to the cathodic chamber, it is known as biocathode (Harnisch & Schro, 2010).

Although practically the recovery of bioelectricity from large-scale MFCs is still low and more research to increase the system's efficiency and storage of the generated electricity is required, the predominant use of MFCs is to treat wastewater along with the production of bioelectricity simultaneously (Vinayak et al., 2023). Furthermore, research has shown that MFCs have higher degradation kinetics for major recalcitrant organic contaminants such as azo dyes, organochlorine compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and certain pesticides, giving them an edge over other conventional treatment methods such as activated sludge systems, anaerobic sludge blankets, and constructed wetland systems (Fang et al., 2013; Fernando et al., 2014; Yang et al., 2019).

4.1 Remediation of azo dyes

Azo dyes are one of the most hazardous recalcitrant pollutants. They belong to the class of xenobiotics and have azo moieties (-N═N-) in their structure, making them highly oxidative in nature. When BESs are used to treat azo dyes, the microorganism in the anodic chamber degrades the cosubstrate, thereby releasing electrons and protons, the electrons reach the cathode via an external circuit, whereas the protons cross the PEM to reach the cathode. These electrons and protons act on the azo pollutants and break them into their constituent colorless and biodegradable aromatic amines, simultaneously generating bioelectricity (Fernando et al., 2019). Research has shown that the half-cell reduction potential for BESs to decolorize hazardous azo dyes effectively ranges from −525 to −175 mV when compared against standard hydrogen electrodes (vs. SHE) (Van Der Zee et al., 2003). Research done by Sun et al. (2009) using glucose and wastewater from the confectionary industry as a cosubstrate for degradation and decolorization of the dye known as active brilliant red X-3B (ABRX3) in a single-chambered MFC with air cathode produced good results along with the simultaneous generation of electricity.

In comparison with conventional anaerobic treatment methods, MFCs have been shown to decolorize ABRX3 much more efficiently. In another study done by Mu et al. (2009) using an abiotic cathode and biotic anode to degrade and decolorize acid orange 7 (AO7) dye, it is reported that decolorization efficiency can reach up to 2.64 ± 0.03 mol/m^3/d along with the generation of bioelectricity. But when power in the form of a steady cathodic potential of −400 mV (vs. SHE) was applied to the cathode, this led to five times increment in decolorization efficiency. Decolorization of another dye, alizarin yellow R (AYR), was studied by Cui (2011) using a double-chambered MFC, where a biocathode containing autotrophic inoculum was applied to degrade the dye. Experimental conditions were optimized, such as pH was maintained

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at 5.3 and 500 mV of voltage was supplied; in a span of 48 h, the efficiency rate of decolorization reached around 99.1% (initial concentration 100 mg/L). The obtained efficiency rate is much higher than the rate generated from studies done with biocathodes inoculated with abiotic and mixed sludge culture.

4.2 Remediation of organochlorine

Organochlorines are highly toxic and recalcitrant organic compounds that contain one or more covalently bonded chlorine atoms and are commonly found in bleaching agents, chlorinated solvents such as perchloroethene (PCE) and trichloroethene (TCE) and pesticides. Vinyl chloride (VC), which forms due to incomplete dechlorination of PCE and TCE, is a potent carcinogen; proper treatment of organochlorides is much needed. Certain anaerobic microorganisms such as *Desulfitobacterium* and *Dehalococcoides* species (DiStefano et al., 1991; Löffler et al., 2000; Yang & McCarty, 1998) have been shown to reduce chlorinated compounds by using hydrogen (H_2) as the final electron donor. However, they compete for electrons from acetate, sulfate, iron (III), and CO_2 reducers. Cathode potential was varied from −250 to −750 mV versus SHE to study the dechlorination of TCE in a BES with an operational time of 570 days (Aulenta et al., 2011). The highest dechlorination occurred at −250 mV when methanogenesis was mainly suppressed, leading 94.8% of accessible electrons to proceed for dechlorination. However, when the cathodic potential dropped below −450 mV versus SHE, methanogenesis consumed about 65% of available electrons, which decreased the TCE dechlorination efficiency of 63 ± 5 μmol/L/d. Dechlorination through BESs has been reported to generate steady and efficient results even on other chlorinated compounds such as chlorophenols and 1,2-dichloroethane (Huang et al., 2011).

4.3 Remediation of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that consist of two or more aromatic rings fused together and are generated due to incomplete combustion of fossil fuels and their derivatives such as gasoline, naphthalene, or phenanthrene. PAHs are insoluble in water but readily dissolve in fat-containing medium, making them bioaccumulate inside living organisms' cells once they enter them through PAH-contaminated soil or water. Studies have shown that crops grown in soils receiving effluents and wastewater from industry or municipality (Cai et al., 2007; Villar et al., 2006) accumulate excess PAHs. Other studies done by Wennrich et al. (2002) showed that vegetables grown in PAH-contaminated soil had bioaccumulated these chemicals inside their cells (Table 14.1). PAHs enter higher living organisms through the food chain and are a potent carcinogenic agent. PAH

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TABLE 14.1 Studies using BES technology to biodegrade various azo dyes, organochlorides, PAHs, and pesticides.

Reactor design	Type of dyes	Inoculum used	Power production	Pollutant production efficiency	References
MFC	Combination of two dyes (reactive red 21 (RR21) and reactive orange 16 (RO16))	*Pseudomonas aeruginosa* 23 N1	941.60 ± 5 mW/m^2	86.5%	(Mishra et al., 2020)
MFC	Reactive orange 16	*P. aeruginosa*	2886 ± 15 μW/m^2	97% ± 1.5%	(Ilamathi et al., 2019)
MFC	Reactive black 5	*P. aeruginosa*	1905 ± 8 μW/m^2	96% ± 1%	(Ilamathi et al., 2019)
BES having glassy Carbon electrode modified with methyl-viologen	Trichloroethene (TCE)	Mixed culture dominated with *Dehalococcoides* spp.	–	0.001 (mol/m^3/d)	(Aulenta et al., 2007)
MEC acetate in the anode, 2-chlorophenol in the biocathode	2-Chlorophenol	Anaeromyxobacter dehalogenase	–	0.04 (mol/m^3/d)	(Strycharz et al., 2010)
MFC/MFC + anoxic cathode	Petrochemical Wastewater (BOD 5/COD: 0.36)	Mixed culture (aerobic + anaerobic)	17.2 mW/m^2 (anoxic), 14.5 mW/m^2 (aerobic)	–	(Yeruva et al., 2015)
SMFC	C8-C 40 n-alkanes, 16 PAHs	Geobacteraceae sp. and *Escherichia* sp.	36.5 mW/m^2	–	(Li et al., 2016)
MFC	Oxyfluorfen	Activated sludge	0.8 V OCV	78%	(Zhang et al., 2018)
MFC	Hexachlorobenzene (HCB)	Anaerobic sludge	70.9 mW/m^2	71.15%	(Cao et al., 2017)

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degradation is tedious and usually takes years to degrade as they are fat-loving and water-hating compounds (Jones & Voogt, 1999; Kronenberg et al., 2017).

Conventional physiochemical methods such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis or ozonation to degrade PAHs are not effective and are also costly (Dai et al., 2020; Li et al., 2019). MFCs efficiently treat even recalcitrant PAHs by converting the thermodynamically unfavorable PAH degradation reactions to favorable ones. In MFCs, when microbes used to treat PAHs are in close contact with the electrode, they produce better results (Chandrasekhar & Mohan, 2012). One of the first PAHs degradation experiments done on toluene and naphthalene using *Geobacter metallireducens* was done by Zhang et al. (2010).

This species oxidized toluene into carbon dioxide. When compared with naphthalene degradation, it was shown that in MFC, naphthalene was degraded in 9 days while there was no degradation of naphthalene in control (abiotic control as well as in open circuit control). In another study done by Mohan and Chandrasekhar (2011) with soil MFCs, it was shown that soil MFCs could better target five- to six-ring aromatic PAHs while conventional anaerobic techniques can only degrade two- to three-ring PAHs. In a case study done on natural wastewater by Yeruva et al. (2015) with an initial concentration of 3 g TPH/L (total petroleum hydrocarbons/liter) in liquid media, it was shown that in a span of 17 days, the MFC reached the maximum PAH removal efficiency of 70%. When the liquid medium was replaced with sediment, there was a 12-fold increment in the MFCs' PAH degradation capacity when compared with the degradation efficiency of the same compound in nature (Morris & Jin, 2012).

4.4 Remediation of polychlorinated biphenyls

Another recalcitrant organic pollutant that has high bioaccumulation capacity due to its lipophilic nature is polychlorinated biphenyls (PCBs). PCBs are yellowish oil-based liquids with insulating capability and high thermal durability and are also resistant to flame, acids, oxidation, and hydrolysis. Because PCBs have such qualities, they are highly used in transformers and capacitors (Fitzgerald et al., 2007). The chemical structure of PCBs has two fused benzene rings with several attached chlorine atoms and has around 209 isomeric forms. Besides being bioaccumulated in plants and animals through the food chain, PCBs can also enter the human system through direct contact, inhalation, or even PCB-contaminated food (Carpenter, 2006).

Toxicological studies have shown that PCBs can be led to severe skin irritation and lung and eye infection and are one of the leading causes of cancer (DeCastro et al., 2006). Conventional PCB treatment methods, such as anaerobic degradation, are ineffective due to the lack of terminal electron acceptors like sulfate and nitrate in the anaerobic sludge (Margesin & Schinner, 2001). When augmented with electron acceptors, sediments received

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from anaerobic sludge show better microbiological activity. Thereby, soil microbial fuel cells (SMFCs), a type of BES, are currently being studied for treating and degrading recalcitrant pollutants in soil, such as PCBs (Yan et al., 2012). A study done by Xu et al. (2015) has shown that when surfactants such as sodium dodecyl sulfate (SDS) and Tween-80 are used in the blend of weight ratio (1:1) and mass ratio (50:1), respectively, in combination with SMFCs for degradation of PCBs and total organic carbon (TOC), maximum PCB and TOC removal efficiency of 58.90% and 43.25% occurred around 60 days of operation with the highest voltage and power density generation of 0.822 V and 18.30 W/m^3 study done by Wu et al. (2019) on the degradation of PCB and TOC in SMFC in the presence or absence of nanoscale zero-valent iron. The study showed that the maximum PCB (37.56% removal efficiency) and TOC (49.75% removal efficiency) along with maximum power density generation (108.90 mW/m^2) was achieved when SMFC was used in combination with nanoscale zero-valent iron. The results from these studies show that SMFC can be used effectively for the biodegradation of PCBs during the simultaneous generation of bioelectricity.

4.5 Remediation of pesticides

Pesticides are chemical compounds that mitigate pests and weeds that destroy agricultural crops and plants. The use of pesticides has increased food production on a large scale, but most of the pesticide and their remnant are highly hazardous for nontargeted organisms and cause several diseases such as cancer, kidney and liver failure, neurological disorder, and birth defects (Arya et al., 2021). In addition, the constant use of pesticides led to severe pollution of surface run water, groundwater, and soil. Currently, BESs have been shown to degrade pesticides such as hexachlorobenzene (Cao et al., 2015), isoproturon (Rodrigo Quejigo et al., 2018), and metolachlor (Li et al., 2018) from contaminant soil using SMFC augmented with indigenous microbes, as well as simultaneous production of bioelectricity.

5. Exoelectrogenic microorganisms

Exoelectrogens are microorganisms that have the capacity to transport electrons produced by the oxidation of organic matter from inside of their cells to electron acceptors residing outside of their cells. This transfer and movement of electrons generate electrical energy. These microorganisms are helpful in a variety of remediation and wastewater technologies. Industrial effluent, municipal effluent, anaerobically treated sludge from domestic or industrial wastewater treatment plants, anaerobic sediments, and farm soil are rich sources of these microorganisms. These sources can be used to isolate exoelectrogenic microorganisms. Electrical energy is generated by them from chemical or organic sources such as wastes from domestic, municipal and

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industrial wastewater treatment plans, industrial dyes, marine sediments, lake sediments, and simple carbohydrates such as glucose (Luo et al., 2012). Because of this mechanism, exoelectrogenic microorganisms drive BESs such as desalination cells, MECs, microbial electrosynthesis systems and MFCs.

There is no need to replenish catalysts for organic matter degradation as the microorganisms are self-replicating. However, the use of exoelectrogenic microorganisms is limited to the bioremediation, power generation, seawater desalination, and biosensor industries. The inability to develop biofilms and the ineffective extracellular electron transfer (EET) between the bacteria and electrode are the causes of this. Exoelectrogenic bacteria play a key role in determining the effectiveness of the BES, making it essential for them to thrive and survive at optimal levels.

5.1 Respiration in exoelectrogenic microorganisms

Adenosine triphosphate, or ATP, is the most common kind of energy used by bacteria. Two processes, substrate-level phosphorylation and oxidative or photophosphorylation, account for the majority of the production of ATP. In substrate-level phosphorylation, the formation of ATP can be shown by two different reactions.

$$\text{ADP (adenosine diphosphate)} + \text{substrate-P} = \text{ATP} + \text{substrate} \quad (14.1)$$

$$\text{ADP} + \text{Pi (inorganic phosphate)} + \text{substrate-X} = \text{ATP} + \text{substrate} + \text{X} \quad (14.2)$$

In oxidative photophosphorylation, ATP generation is linked to electron transport processes that can be promoted by light (in phototrophs) or by the oxidation of both organic substances and inorganic ions (in organo-heterotrophs and chemolithotrophs, respectively) that have a negative redox potential. The reduction of electron acceptors with a higher positive redox potential is related to this.

Characterization of these microorganisms is done by various factors such as salt concentration, pH, media, and temperature. The BES's capacity for the decomposition of organic matter and its generation of electrical energy can both be improved with the incorporation of the compatible exoelectrogens. Exoelectrogens can be categorized into a number of functional groups owing to the sort of anaerobic respiration they operate in. These include dissimilatory metal-reducing bacteria (DMRB) such as *Geobacter*, *Shewanella*, *Geopsychrobacter*, and *Geothrix*, sulfate-reducing bacteria (SRB) such as *Desulfuromonas* and *Desulfobulbus*, and nitrate-reducing bacteria (denitrifying bacteria) such as *Pseudomonas* and *Ochrobactrum*. Furthermore, it has been discovered that anaerobic respiration pathways are carried out by fermentative bacteria that include *Clostridium* and *Escherichia coli*, purple nonsulfur

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bacteria, nonphotosynthetic *Rhodoferax ferrireducens*, and photosynthetic *Rhodopseudomonas palustris* DX-1 to produce electricity.

Only until the final electron acceptors in the electron transport chain (ETC) have used all of the available electrons to generate ATP is cellular respiration deemed to be complete. In aerobic respiration for substrate-level phosphorylation, electron acceptors can be other soluble substances such as iron (Fe) or manganese (Mn) in the form of their oxides or molecular oxygen in oxidative phosphorylation. Fig. 14.1 shows the representation of catabolic and respiratory pathways in an exoelectrogenic cell. The organic substrate is absorbed by the cell of the electrogenic microbe. After that, the substrate passes through a catabolic reaction, such as glycolysis. In addition to producing intermediate products such as pyruvate, this reaction also releases electrons. Pyruvate is converted to acetyl CoA, which then participates in the Kreb's and electron transport cycles to release more electrons while acting as an anode for the ultimate electron acceptor.

Exoelectrogenic bacteria are required for BESs to function by colonizing the electrode or forming a biofilm on it. The electrode serves as the ultimate electron acceptor in the microbial oxidation of organic materials in the anodic chamber. Since the final electron acceptor, which is typically oxygen or other naturally occurring metal ions of iron or manganese, is located outside the cell, this electron transfer is exogenic and is therefore known as exoelectrogenic (Fig. 14.1). By absorbing the electrons that move from the anode to the cathode along the circuit, the electron acceptors in the cathode chamber are reduced.

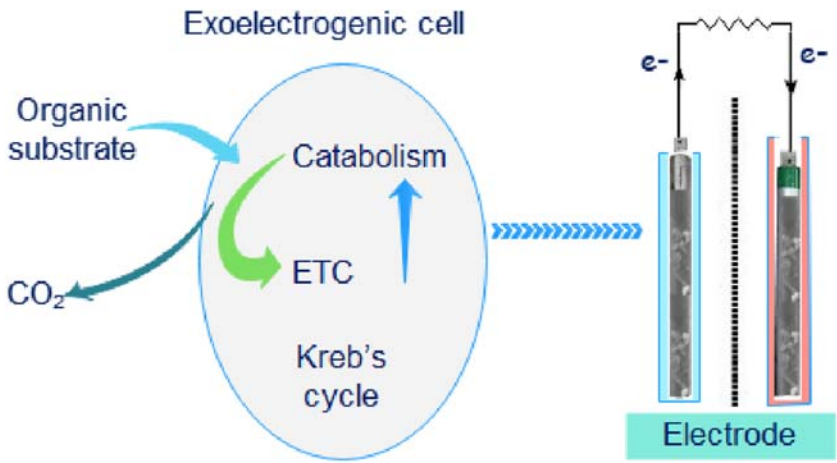

FIGURE 14.1 Schematic representation of catabolic and respiratory pathways in an exoelectrogenic cell.

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Exoelectrogenic bacteria predominantly transmit electrons to the anode in four processes:

(a) Employing C-type cytochromes to transmit electrons directly from the cells to the anode:

The proteins, such as outer membrane cytochromes (OMCs), enable this technique. The c-type cytochromes are one class of OMCs. The outer membrane c-type cytochrome gene expression is particularly stimulated by the high-potential electrode. As a result of the substantially lower number of electrochemically active bacteria in contact with the anode in this approach, the current density is constrained. Therefore, current production will be limited to this monolayer biofilm.

(b) Solid conductive components, such as pilli or nanowires:

Bacterial nanowires, which are electrically conductive pili and exopolymeric substances that act as semiconductors, allow electron transfer from inside the cell to its outside. By using this technique, the electrons can create a substantial biofilm and move through the exopolymeric and pilli-created matrix. This method is recognized as the most effective way for optimum bacteria growth and high current densities.

(c) By forming an electroactive biofilm:

A self-produced polymeric matrix on the surface is known as biofilm. The electrons in the biofilm travel via cells close to one another until they arrive at the electrode. It has been noted that a thick electroactive biofilm generates the most power in a BES.

(d) Employing soluble electron shuttles:

These small mediator compounds take in the respiration-generated electrons and secrete them so they can travel to the anode and transfer electrons there. These can be chemically manufactured but are also endogenously produced by cells. The cell-produced electron shuttles are found to be more efficient than those made chemically. A few electron shuttles produced by the cells are phenazines and flavins. The limitation of using endogenously produced electron shuttles is the slow diffusion of these electron shuttles. To overcome this limitation, high concentrations of electron shuttles should be produced.

The exoelectrogenic microorganisms consume the organic or chemical substrates to produce electrons. And the flow of these electrons in a BES produces potential differences and, ultimately, electric current. The BESs can be used for two purposes at a time. One is the production of electrical energy, and the other one is the degradation or remediation of the substrate by using microorganisms as biocatalysts, hence the names biodegradation or bioremediation, respectively. Exoelectrogenic microorganisms are substrate specific.

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Depending on the substrate, a particular species or a few species of exoelectrogenic microorganisms become predominant in the BES. In Luo et al. (2012), it was reported that a mixed culture containing Proteobacteria as the dominating species removed 55% of chemical oxygen demand (COD) from wastewater. Another study found that Actinobacteria were the major species in the 52% COD reduction from municipal wastewater. In Shinde et al. (2018), *Pseudomonas putida* was used to treat wastewater from a steel plant in activated sludge at the anode chamber, and 70% COD reduction was seen. To improve the efficiency of COD removal when using pure cultures in BESs, their substrates must be precisely identified. The substrate specificity and successful operation of the exoelectrogenic bacteria are demonstrated by all of the aforementioned examples.

6. Conclusions and prospects

Electrochemistry is vital in sustainable bioremediation and has been extensively investigated for removing various toxic organic and inorganic pollutants. Advances in electrochemical technologies integrating various microbes to degrade contaminants from the environment have several advantages over established pollutants remediation technologies. BES works on the electrochemistry principle, simultaneously treating various types of contaminants through redox potential difference between the anodic oxidation and cathodic reduction reactions. This technology provides an efficient and sustainable way to remove pollutants from soil, water, and air, allowing the construction of a simple, compact, or even modular bioremediation process. It requires little maintenance compared with other bioremediation technologies and can be easily scaled up. BES technologies enhance the bioremediation process and have a better prospect of producing bioelectricity. BES is also now used to produce biohydrogen, biomethane, value-added products, and other valuable chemicals. BESs-based biosensors have emerged as unique tools for pollutants. Combining electrochemical technologies with other technologies has shown opportunities for efficient metal recovery from polluted environments. However, much progress has been made in improving electrochemical technologies in recent years for removing pollutants and metal recovery from polluted environments, but there are still challenges for future research.

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Advances in Environmental Electrochemistry

Edited by Dipak Ashok Jadhav, Manaswini Behera, Surajbhan Sevda, and Maulin P. Shah

Advances in Environmental Electrochemistry provides a solid foundation in the basics of environmental electrochemistry, including redox reactions for contaminant removal, bio-electrochemical systems, electrochemical reactor design and the various electrochemistry-based techniques for practical wastewater degradation, environmental remediation and bioenergy recovery from waste. Advanced technologies acting as key indicators for addressing the various aspects of environmental electrochemistry are covered as well as comparisons to conventional methods and potential ways forward to their application in bioremediation technology. This book will be of interest to chemical engineers, environmental engineers, and all those interested in environmental biotechnology, bio-electrochemical systems, electrochemical sensors, advanced oxidation processes, biological wastewater treatment, and waste to energy recovery.

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