



Review

Applications of Emerging Bioelectrochemical Technologies in Agricultural Systems: A Current Review

Simeng Li 1,* D, Gang Chen 1 and Aavudai Anandhi 2 D

- Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering, 2525 Pottsdamer Street, Tallahassee, FL 32310-6046, USA; gchen@eng.famu.fsu.edu
- Biological Systems Engineering, Florida Agricultural and Mechanical University, Tallahassee, FL 32307, USA; anandhi@famu.edu
- * Correspondence: sl16b@my.fsu.edu; Tel.: +1-850-645-0126

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Abstract: Background: Bioelectrochemical systems (BESs) are emerging energy-effective and environment-friendly technologies. Different applications of BESs are able to effectively minimize wastes and treat wastewater while simultaneously recovering electricity, biohydrogen and other value-added chemicals via specific redox reactions. Although there are many studies that have greatly advanced the performance of BESs over the last decade, research and reviews on agriculture-relevant applications of BESs are very limited. Considering the increasing demand for food, energy and water due to human population expansion, novel technologies are urgently needed to promote productivity and sustainability in agriculture. Methodology: This review study is based on an extensive literature search regarding agriculture-related BES studies mainly in the last decades (i.e., 2009-2018). The databases used in this review study include Scopus, Google Scholar and Web of Science. The current and future applications of bioelectrochemical technologies in agriculture have been discussed. Findings/Conclusions: BESs have the potential to recover considerable amounts of electric power and energy chemicals from agricultural wastes and wastewater. The recovered energy can be used to reduce the energy input into agricultural systems. Other resources and value-added chemicals such as biofuels, plant nutrients and irrigation water can also be produced in BESs. In addition, BESs may replace unsustainable batteries to power remote sensors or be designed as biosensors for agricultural monitoring. The possible applications to produce food without sunlight and remediate contaminated soils using BESs have also been discussed. At the same time, agricultural wastes can also be processed into construction materials or biochar electrodes/electrocatalysts for reducing the high costs of current BESs. Future studies should evaluate the long-term performance and stability of on-farm BES applications.

Keywords: bioelectrochemical system; agriculture sustainability; electricity generation; resource recovery; desalination; agricultural monitoring; biochar

1. Introduction

Energy is an important and necessary input for today's increasingly mechanized agriculture. Farm production, for both crop and animal products, requires direct use of energy as fuel or electricity to operate diverse farm machinery and equipment and maintain other agricultural activities (Table 1), and also indirect use of energy due to the consumption of fertilizers and pesticides. The supply and demand of energy in agricultural systems can significantly impact the profitability of agriculture [1]. At the same time, excessive use of fossil fuels, fertilizers and pesticides, etc. in crop production, as well as the misuse of antibiotics in livestock production, can result in many environmental problems such as

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greenhouse gas emission and water body contamination [2–4]. In addition, many agricultural systems produce a vast amount of different waste materials that need to be appropriately treated or disposed [5]. These agricultural wastes, such as stover and livestock manure, usually contain large amounts of microbially degradable organic matter [6]. In response to the call for improving sustainability in agriculture, a variety of environment-friendly technologies that utilize agricultural wastes for energy production or resource recovery have been recently developed and applied in agricultural systems, among which bioelectrochemical systems (BESs) seems to be the most promising [7].

Table 1. Direct energy uses in agricultural production.

Uses of Energy	Types of Energy	
Operating agricultural machinery and large trucks Operating small vehicles	Diesel Gasoline	
Irrigation; crop processing; heating/cooling; animal waste treatment	Diesel; natural gas; liquified petroleum gas; electricity	
Power for farm houses and facilities	Electricity	

As hybrid systems of microbiology and electrochemistry, BESs are able to produce electrical energy or various value-added chemicals via different microorganism-catalyzing redox reactions [8]. Like in other types of electrochemical systems (e.g., batteries), electricity is automatically generated when the redox potential of the reduction half-reaction on the cathode is larger than that of the oxidation half-reaction on the anode. Otherwise, the flow of electrons can be driven by external power in order to impel desired redox reactions for resource recovery [7]. Because BESs are able to use diverse biodegradable organics as electron donors, simultaneous degradation of these organics can be effectively achieved as well [9]. Depending on the diverse end objectives, BESs generally vary greatly in reactor configurations, dimensions, substrates, bacterial communities, etc. [7]. In spite of the various differences, BESs are usually classified according to their application purposes (Figure 1) and can be divided into microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial electrosynthesis (MESs), microbial desalination cells (MDCs), microbial solar cells (MSCs), and enzymatic biofuel cells (EFCs) [8]. The components, mechanisms and applications of these different types of BESs are briefly discussed in the next section.

Over the last decade, considerable efforts have been made to advance the performance and applicability of emerging BESs focusing on treating domestic and industrial wastewater, and a lot of significant progress has been achieved [9]. However, in comparison, applications of BESs in agriculture have received much less attention. There is also a lack of state-of-the-art reviews on the applications of BESs in agricultural systems. Therefore, this article presents a critical review on the past studies of BESs with an emphasis on the applications related to agriculture. Moreover, with the discussion on the current and future applications of different BESs in agricultural systems, this article also aims to draw a blueprint of future sustainable agricultural systems tackling the nexus of food, energy and water using emerging BES technologies. The rest of the paper is structured as follows: Section 2 describes the methodology used for this review study; Section 3 provides brief introductions of different types of BESs; Section 4 summarizes diverse agricultural applications of BESs that are currently available; Section 5 discusses various agricultural applications of BESs that are potential in the future.

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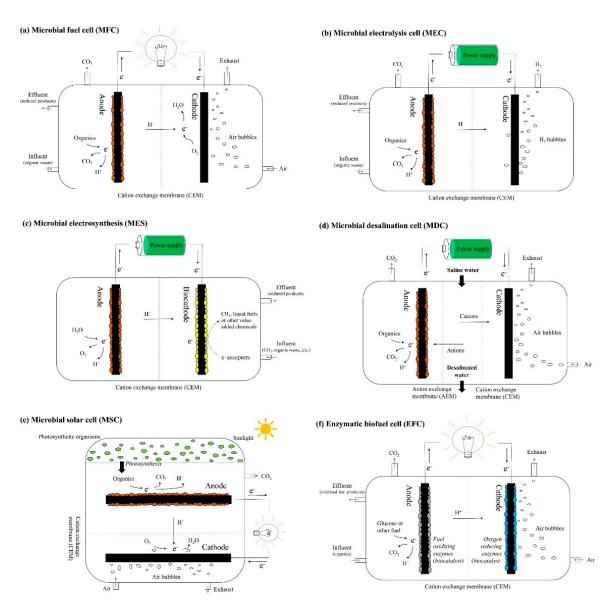


Figure 1. Different bioelectrochemical systems (BESs) classified by application purposes.

2. Methodology

This review study is based on an extensive literature search regarding agriculture-related BES studies mainly in the last decade (i.e., 2009–2018) (Figure 2). Three potent databases, Scopus, Google Scholar and Web of Science, were utilized to locate and access the literature, respectively. Appropriate search terms and time ranges were defined within each database. For example, in order to find literature on the applications of MFC in agriculture, a general search term "microbial fuel cell AND agriculture" was first used. Afterwards, more specific search terms such as "microbial fuel cell AND animal wastewater" were also used. The process was repeated with various relevant search terms until no additional studies were found. The time range was first set for 2009–2018. However, under situations where the number of studies returned from the search was small, the time range was then extended for 1999–2018. The cut-off date for publications that were included in this review study was 31 September 2018. The search results were carefully selected because many of the studies were either unable to provide sufficient information or the information was irrelevant. In addition, only peer-reviewed literature was selected for this work. The discussion of current applications of BESs in agriculture were completely based on the information and data collected from the literature. Whereas, agricultural applications of BESs in the future were discussed according to both peer-reviewed literature and

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science-based reasoning. Whenever necessary, relevant data that were presented graphically were extracted using free-access DataThief III.

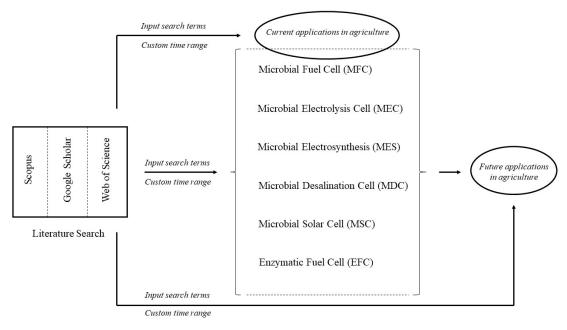


Figure 2. Rationale of methodology.

3. Types of BESs

3.1. Microbial Fuel Cells (MFCs)

MFCs (Figure 1a) are the most fundamental BESs and have been extensively investigated towards real-world applications [10,11]. With electrochemically active bacteria (i.e., exoelectrogens) such as *Geobacter sulfurreducens* and *Shewanelle putrefaciens* on the anode, MFCs are able to generate electrical energy directly from a broad range of biodegradable organics through different redox reactions on the electrodes [12]. In MFCs, the organics in the anode compartment serve as electron donors when they are consumed by exoelectrogens, which produce extracellular electrons that can be collected from the anode. Through an external circuit, the electrons flow to the cathode, thus forming an electric current that can be harnessed for immediate usage or stored for later [8]. The development of air-cathode MFCs has made this technology more feasible to treat wastewater and harvest electricity in practice [13]. Many studies, including some pilot studies [13–15], have reported considerable electric power generation from domestic wastewater [16], industrial wastewater [9], landfill leachate [12], and swine wastewater [17], etc. However, the high cost of the electrodes and the diminished power at larger scales are the two main factors limiting the commercial applications of larger-scale MFCs [13].

3.2. Microbial Electrolysis Cells (MECs)

Adapted from MFCs, MECs are capable of producing hydrogen gas (H₂), methane (CH₄) or other value-added chemicals for indirect energy usage and storage [8]. Theoretically, MECs are able to produce any value-added chemicals regardless of the redox potential differences on the electrodes [18]. The thermodynamic barriers for accomplishing required redox reactions are resolved by driving the electron flow with external electric power (Figure 1b). In order to maximize the usage efficiency of electrons for the production of desired products, the cathode compartment needs to be maintained as anaerobic or anoxic. Among the products that can be produced in MECs, H₂ has demonstrated very promising commercialization potential as a renewable energy, considering the convenience for storage and transportation, as well as the rapidly increasing market demand of H₂ [19]. The system efficiency of MECs is significantly higher than that of other BESs [18], and therefore, more and

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more research attention has been focused on producing H_2 in MECs using a variety of wastes and wastewater [20–23]. During the recent years, remarkable advances in MEC-based H_2 production have been reported, with H_2 yield (i.e., moles of produced hydrogen per moles of consumed substrate, or mass of produced hydrogen per mass of consumed substrate) raised from less than 50% to nearly 100%, and H_2 production rates elevated from below 0.1 m³ H_2/m^3 reactor/day to as high as 50 m³ H_2/m^3 reactor/day [18].

3.3. Microbial Electrosynthesis (MESs)

As a novel perspective of BESs, MES (Figure 1c) is a form of microbial electrocatalysis that can produce value-added products (e.g., acetate, butyrate, ethanol, and biodiesel, etc.) by electric power-driven reduction of CO₂ and other organics at the biocathode using microorganisms as a biocatalyst [24]. Given appropriate biocatalysts, electron acceptors and redox mediators, the value-added products produced in MESs can be highly specific [25]. Notably, depending on the feeding substrates, various industrially relevant products such as bioethanol, biofuel and bulk chemicals can also be produced via oxidation reactions at the anode in MESs [24]. The feeds suitable for MESs are similar to those reported for MFCs, but external electric power is utilized in MESs to generate organics [26]. As such, the processes in MESs are opposite to those employed in MFCs, and energy is stored in covalent chemical bonds instead. At the same time, it should also be noted that MESs are related to (but different from) MECs, in which the external electric power provides additional electrical potential to make it sufficient for the reduction reactions at the cathode, e.g., reduction of H⁺ to H₂ [27]. MESs have a significant diversity of applications, as the various end products include but are not limited to different types of biofuels [28], industrially relevant chemicals [29] and drug precursors [30], etc. Therefore, many researchers believe that the role of MESs in future bioproduction will be increasingly important [30].

3.4. Microbial Desalination Cells (MDCs)

MDCs have been modified from MFCs to cut down the high energy demand of commonly used desalination technologies (e.g., reverse osmosis, electrodialysis and mechanical vapor compression, etc.) [31]. In MDCs, a desalination compartment equipped with a cation exchange membrane (CEM) and an anion exchange membrane (AEM) is inserted in between the anode and cathode compartments (Figure 1d). Driven by the electrochemical potential differences between the electrodes, the cations and anions flow through the CEM and AEM into the cathode and anode compartments, respectively [32]. As a result, the saltwater is desalinated with the losses of ions. At the same time, the electrical energy recovered from the organics in the anode compartment can be utilized or stored elsewhere. High desalination efficiency of 90%, together with a maximum power density of 31 W/m³, has been observed with the use of acetate as an electron donor and ferricyanide as an electron acceptor [31]. Further studies have shown that domestic wastewater as an electron donor and sparged air as an electron acceptor could also achieve considerable salinity removal of over 60% [33]. Due to the advantages of treating wastewater and desalinating saltwater simultaneously in a single device while retrieving electric power from these processes, MDCs have been widely considered as a promising energy-efficient technology to address emerging challenges, including saltwater and brackish water desalination, value-added chemical production, groundwater remediation, wastewater treatment, and energy recovery [31,34–36].

3.5. Microbial Solar Cells (MSCs)

MSCs are BESs that can recover in-situ bioelectricity or value-added chemicals by integrating photosynthesis and exoelectrogenesis [37]. MSCs (Figure 1e) use photosynthetic organisms such as photoautotrophic microorganisms or higher plants to convert solar energy to chemical energy in organic matter, which is further utilized by MFC components to generate electricity. The key process in an MSC is the transport of the organic matter produced from photosynthesis to the anode

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compartment. There are generally three modes of transfer, i.e., through the rhizodeposition of a high plant, through the diffusion of a phototrophic biofilm, or through the pumping for translocation from a photobioreactor or coastal marine ecosystem [37]. Among the various types of MSCs, those integrated with living higher plants (a.k.a., plant microbial fuel cells (PMFC)) have demonstrated the most effective power generation as high as 1000 GJ/ha/year (i.e., 3.2 W/m²), as estimated by recent studies [37–39]. The power generation from PMFCs has been found directly related to the availability of rhizodeposits for anodic oxidation reactions [7]. Unlike conventional solar cells, MSCs are able to generate not only electricity, but also a great diversity of value-added chemicals [40]. Benefitting from the continuously growing population of microorganisms carrying out the photosynthetic and electrochemical reactions, MSCs are self-repairing systems with a longer lifetime and lower maintenance [37]. The applications of MSCs are broad and promising because they are compatible with many different systems as sustainable and eco-friendly energy suppliers or biosynthesis reactors [41].

3.6. Enzymatic Biofuel Cells (EFCs)

EFCs utilize specific oxidoreductase enzymes as electrocatalysts to convert the chemical energy stored in organic matter into directly usable electrical energy with the oxidation reactions at the anode and reduction reactions at the cathode (Figure 1f). In early EFCs, enzymes were used in the electrolyte suspension but the systems were plagued by low performance and stability [42]. Recent studies have developed different techniques to immobilize and stabilize enzymes at the electrode surface [43]. For example, crosslinking redox hydrogels, as well as sandwich and encapsulation techniques, have been used to entrap enzymes while allowing for uninterrupted transport of organic matter within the compartments [44]. At the same time, to improve the system stability of EFCs, biocatalysts from thermophilic microorganisms have been widely investigated considering their better thermal stability under higher operation temperatures [45–47]. With the rapid development in recent years, EFCs have been applied to power biosensors and portable devices [46,48–50], as well as implantable systems [51–53]. Researchers have also been actively excavating the potential of EFCs for energy conversion and storage from different sources [46].

4. Current Applications of BESs in Agriculture

4.1. Direct Generation of Electric Power

Among the different BESs, MFCs have been widely studied in many countries to treat a diversity of agricultural wastes and animal wastewater while simultaneously generating sustainable bioelectricity that can be directly utilized as on-farm electric power supply [17,54–57]. The resulting electric power varied depending on the type and concentration of feed, as well as the type of MFC reactor (Table 2). For example, with swine wastewater containing 8320 ± 190 mg/L of soluble chemical oxygen demand (SCOD), Min et al. [17] obtained a maximum power density of 45 mW/m² using a two-chamber MFC with an aqueous cathode but a significantly higher maximum power density of 261 mW/m² using a single-chamber air-cathode MFC. However, a later study using the same type of MFC (i.e., single-chamber air-cathode) to treat less concentrated swine wastewater $(1820 \pm 83 \text{ mg SCOD/L})$ only achieved a relatively lower maximum power density of 205 mW/m^2 [56]. In addition, lignocellulosic biomass such as corn stover and wheat straw has also been investigated as possible feed for MFCs [58-60]. For instance, Wang et al. [58] used both raw and steam-exploded corn stover to feed single-chamber air-cathode MFCs and observed considerable maximum power densities of 296 and 343 mW/m², respectively. In addition, wastewater from agriculture-relevant industries, e.g., rice mill wastewater [61] and food-processing wastewater [62], has also been identified as potential feed for effective electricity generation in MFCs. However, despite the continuous progress in using agricultural wastes and wastewater to feed MFCs, the electricity production with these applications is often challenged by the occurrence of other microbial processes such as methanogenesis (i.e., the generation of methane) and ammonification (i.e., the conversion of organic nitrogen to

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ammonia) [17,55]. In MFCs, the reduction of carbon dioxide to methane in the anode compartment consumes electrons, thus decreasing the Coulombic efficiency and lowering the power generation [10]. Also, high concentrations of ammonia are toxic to most exoelectrogens that power MFCs [63]. Therefore, in order to maximize the electricity recovery from agricultural wastes and wastewater, future efforts need to be focused on minimizing the negative impacts of methanogenesis and ammonification on MFC performance.

MSCs, or more specifically, PMFCs, [64] have also attracted research attention in the recent years for their potential to generate electricity from the rhizodeposits, i.e., organic compounds (e.g., sugars, organic acids, polymeric carbohydrates, enzymes, and cellular debris, etc.) excreted from plant roots [37]. Some MSC studies have integrated the MFC anode into the plant-growing soil, where the rhizodeposits from the plants and organic matter from the soil were available for electricity production [65–67]. The electricity production by a PMFC in practice has been conservatively estimated to be 21 GJ ha⁻¹ year⁻¹ (equivalent to 67 mW/m²) [68]. Significantly higher power generation of 300 mW/m² has been observed in laboratory-scale experiments harvesting electricity from rhizodeposits of rice plants [67]. A long-term PMFC study conducted using *S. anglica* generated an average power generation of 50 mW/m² [64], in which it is possible to be greatly improved by a change of the ion transport direction within the bioelectrochemical reactor [69]. To advance the research and practical applications of PMFCs, the principal processes must be further understood. Mechanistic models also need to be established to optimize the design of system constituents and operation conditions [37].

Table 2. Electric power generation in microbial fuel cells (MFCs) using different types of agricultural wastes/wastewater.

Type of Feed	Concentration (mg SCOD/L)	Type of MFC	Power Generation (mW/m²)	Reference
Swine wastewater	8320	Two-chamber; aqueous cathode	45	[17]
Swine wastewater	8320	Single-chamber; air-cathode	261	[17]
Swine wastewater	1820	Single-chamber; air-cathode	205	[56]
Dairy manure wastewater	450	Single-chamber; air-cathode	189	[70]
Cattle manure leachate	4000	Two-chamber; air-cathode	216	[71]
Cattle manure slurry	2500	Cassette-electrode; air-cathode	163	[72]
Raw corn stover	1000	Single-chamber; air-cathode	296	[58]
Steam-exploded Corn stover	1000	Single-chamber; air-cathode	343	[58]
Steam-exploded Corn stover	1000	Single-chamber; air-cathode	371	[59]
Wheat straw	2000	Two-chamber; aqueous cathode	123	[60]

4.2. Production of Biohydrogen

Many different types of agricultural wastewater such as dairy manure slurry [73], swine wastewater [74] and fermentation effluent [75] have been used for the production of biohydrogen in MECs (Table 3). Comparing with other biohydrogen technologies such as anaerobic digestion and photobiological processes, MECs have demonstrated better performance in producing H₂ from more diverse substrates because of its ability to overcome thermodynamic limitations [18,76]. However, the performance of MECs, in terms of the H₂ production rate and H₂ yield, varies when different substrates were used for the conversion [77]. Highest H₂ production rate up to 50 m³/m³/day and H₂ yield of nearly 100% have been reported for MECs utilizing readily biodegradable organics such as acetate and other fermentation products from anaerobic digesters [18]. For the same MEC system using the same substrate, the application of a higher external voltage typically results in higher H₂ production rate and H₂ yield because of the improved electron transfer towards the cathode driven by the increased voltage. However, a higher external voltage typically decreases the energy efficiency because there is a need for more energy input. It has been reported that the H₂ production and energy efficiency could be balanced with an optimal external voltage of 0.6–0.8 V [76]. At the same time, external voltages supplied by renewable electric power from MFCs and other sustainable power sources can also be utilized to operate MECs [78].

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Anaerobic digesters are fermentation facilities commonly used for the minimization of agricultural wastes and recovery of useful biogases such as H₂ and CH₄ [79]. The integration of MECs with anaerobic digesters have achieved enhanced H₂ production rate and yield [18]. The fermentation in anaerobic digesters can break down large-molecular-weight carbohydrates into small-molecular-weight metabolites that are more readily biodegradable for MECs. The CO₂ produced during the fermentation processes can be recirculated through electrolytes for pH buffering [80]. With the substrates generated from fermentation, MECs can be configured to produce high-purity H₂ under variable operational conditions [81]. So far, using integrated systems, the highest H₂ production rate of 189 m³/m³/day has been reported by Lo et al., which is nearly four times the H₂ production rate using MECs alone [82]. The integration of MECs also completes the oxidation of organics into CO₂ which fermentation alone cannot achieve. The integrated systems were capable of producing H₂ effectively from lignocellulosic materials that are traditionally considered as recalcitrant agricultural wastes, including corn stover, sugar beet, plant leaves, and corn stalk, etc. [83–86]. When combined with fermentation, the average overall increases of H₂ production rate and yield were 148% (ranging from 42 to 538%) and 225% (ranging from 2 to 400%), respectively [18]. The matching between fermentation and electrohydrogenesis rates is the key to further improvement in the system performance, which can be achieved through specially designed feeding strategies or novel stepwise processes [76]. Although long-term pilot studies of MECs have been conducted, larger-scale MECs have not been built up yet, mainly due to economic concerns from the expensive costs of electrodes and external energy inputs [87–89]. In practice, relatively more inexpensive renewable power sources for H₂ production in MECs could be wind, geothermal and hydropower, etc.

Table 3. H_2 production in microbial electrolysis cells (MECs) from different types of agricultural wastes/wastewater.

Type of Feed	MEC Volume (mL)	Applied Voltage (V)	H ₂ Production Rate (m ³ /m ³ /day)	Overall H ₂ Yield (%)	Energy Efficiency (%)	Reference
Corn stalk	64	0.8	3.43	64	166	[90]
Wheat straw	210	0.7	0.61	64	NA	[91]
Swine wastewater	28	0.5	0.9-1.0	17-28	58-74	[92]
Potato wastewater	28	0.9	0.74	73	NA	[70]
Switchgrass wastewater	16	1.0	4.3	50-76	149-175	[93]
Fermentation effluent	26	0.6	2.11	96	287	[94]
Fermentation effluent	64	0.9	4.55	51	185	[95]

4.3. Production of Biofuels and Other Value-Added Chemicals

Besides direct energy recovery in the form of electricity using MFCs and H₂ using MECs, organic-rich agricultural wastes and wastewater have also been used for the production of biofuels and other value-added chemicals in MESs [24]. With the use of CO₂ and clean water, MESs are capable of converting agricultural and forestry residues (e.g., corn stalk, stover, wood, grass, leaves, immature cereal, etc.) into syngas [29], H₂ [96], CH₄ [97], formic acid [98], ethylene [24], methanol [99], dimethyl ether [100], urea [7], succinic acid [101], etc. Through mineralization reactions, CO₂ can also be synthesized into precursors of polymers and carbonates for construction applications [102]. With appropriate redox reactions at the anode and cathode, as well as adequate external input to balance the potential difference, MESs are able to produce many other value-added chemicals including biofuels such as bioethanol and biodiesel [7,103]. Sadhukhan et al. have summarized the equations and Gibbs free energies of 63 anode reactions, 72 cathode reactions and 9 metabolic pathways in MESs that could be used to assess the technical feasibility or thermodynamic spontaneity of resource recovery from wastes and wastewater and combinations of redox reactions [24].

Agricultural residues are abundant and renewable organic feeds for MESs. However, most agricultural biomass are lignocellulosic, meaning a complex mixture of structural polysaccharides such as cellulose and hemicellulose encased by lignin (main constituent of plant cell walls) that is recalcitrant to microbial oxidation [104]. Therefore, oftentimes agricultural residues must be

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fractionated or pretreated to derive monosaccharides or other small-molecular-weight compounds before they can be utilized by microorganisms in MESs to produce value-added chemicals [29]. At the same time, cellulose and hemicellulose can be recovered during the pretreatment and be further processed to produce many different industrial chemicals such as xylite, L-arabinose, furan resins, and nylons, etc. [24]. Lignin can also be recovered to produce wood adhesives, epoxy resins, fuel additives, binders, carbon fiber, and precursors for pharmaceuticals and fragrances [24]. Low-strength agricultural wastewater processed from wheat bran, sugar cane bagasse, coffee husk, pineapple waste, or carrot, etc., as well as stillage streams from on-farm biorefinery processes and fermentation effluent, are suitable substrates in MESs [96]. The biodegradability of the substrate decides the efficiency of usage by the microorganism. The microbial conversion of lignocellulosic biomass typically undergoes hydrolysis, acidogenesis, acetogenesis, and methanogenesis chronologically [12], among which acetogenesis is able to match well with the bioelectrochemical processes and optimize the electron generation at the anode. On the cathode side, electrons donated from the organics can reduce CO₂ to produce targeted organic chemicals. Over the last few years, BES technologies such as MECs and MESs have also been developed to recover metals from wastewater in a less destructive and disruptive manor [7]. Comparing to conventional metal recovery technologies using chemical precipitation, BES technologies, besides their significant metal selectivity, can greatly improve the efficacy and reduce costs from startup, operation and maintenance [105]. In addition, these BES technologies can be integrated with diverse agricultural and industrial systems for selective syntheses of value-added products [24], thus increasing the overall sustainability and economic significance.

4.4. Removal and Recovery of Nutrients

Agricultural wastewater such as animal wastewater is abundant in recyclable nutrients. Animal wastewater with high concentrations (>500 mg/L) of organic nitrogen (N) and ammonia (NH₃) is usually inhibitory to anode-respiring activities and is undesirable for wastewater treatment [106], but with appropriate pretreatment and enhanced reactor designs, the removal and recovery of N in forms of NH₃, NH₄⁺ and NO₃⁻ from N-rich wastewater streams can be effectively achieved with the applications of BES technologies [7,107]. Using recently developed denitrifying biocathode in MFCs or MECs, the removal of NO_3^- can be easily realized by using NO_3^- as the electron acceptor at the electron-donating cathode to generate N₂ (i.e., bioelectrochemical denitrification), which is accompanied with simultaneous generation of electricity or H₂, respectively [108]. However, the removal of NH₃ or NH₄⁺ in BESs is mainly through conventional physical separation or nitrification because the thermodynamic kinetics for anaerobic ammonium oxidation (i.e., Anammox) process are very slow [109]. Therefore, aerobic process has been incorporated into MFC or MEC systems for nitrification that converts NH₄⁺ to NO₃⁻, followed by anaerobic denitrification that reduces NO₃⁻ into N₂ at the biocathode [110]. In addition, BESs integrated with algae growth has enhanced the efficiency of N removal and achieved high nitrogen removals of over 87%, and is greatly attributed to the assimilation of nutrients through photosynthetic metabolisms [111]. Recent BES studies have also discovered that bioelectrochemical reactions can drive NH₃ or NH₄⁺ to be separated from the analyte and migrate/diffuse into the catholyte across the cation exchange membrane (CEM), which led to the discovery of NH₃ recovery using BES technologies [112].

In agricultural systems, recovering nutrients from wastewater is more sustainable than removing them, as the recovered nutrients can be used to fertilize farmlands that are suffering from nutrient depletion. N is one of the most important and necessary plant nutrients [4]. N recovery in BESs is mainly through NH₃ recovery driven by the generated electric current, although N can also be recovered through assimilation and stored in algal cells using algae-containing systems [112]. The NH₃ in the analyte can transport via both migration and diffusion across the CEM to the catholyte, where NH₃-N up to several grams per liter can be accumulated [113]. The NH₃ recovery efficiency can be nearly 100% in some BESs [107]. The high pH of the catholyte can stimulate the generation of NH₃, which can be stripped from the catholyte and captured in an acid solution for producing

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N nutrients later. Similar to MFCs which generate electricity while recovering NH₃, MECs can produce H₂ simultaneously. A recent study reported up to 96% recovery of NH₃ with considerable H₂ generation using MECs that were fed with wastewater containing high concentrations (approximately 1000 mg/L) of NH₃ [113]. The rate of N recovery is similar to that in conventional biological processes (e.g., nitrification and denitrification), which is probably because of the similar microbial redox processes involved for the conversions [112].

In addition to N, other important plant nutrients such as phosphorus (P) and potassium (K) can also be recovered from agricultural wastewater in BESs, depending on the richness of the target nutrient in the raw wastewater [7]. For example, high recovery efficiencies of P ranging from 58 to 92% have been observed in MFCs integrated with algal photosynthesis [112]. At the same time, BES operation can also create a high-pH zone near the cathode to improve struvite precipitation [114]. The main advantages of using BESs for nutrient recovery include the lower demand for input of organics, simultaneous energy generation (either as electricity or H₂), less negative impacts on environment, and good compatibility with other systems, etc.

4.5. Treatment of Agricultural Wastes and Wastewater

Most agricultural wastes and wastewater, especially highly concentrated animal wastes and wastewater, need to be treated before they can be disposed/discharged or merged into domestic wastewater streams for further treatment in wastewater treatment plants (WWTPs) [57]. Solid animal wastes are usually handled by composting or anaerobic digestion, but they can also be effectively treated in BESs to retrieve resources or energy as a bonus [10]. The removal of chemical oxygen demand (COD) is an indicator for the removal of organics during wastewater treatment. Considerable COD removal as high as 98% in BESs treating different types of agricultural wastewater has been widely reported (Table 4). BESs have also demonstrated effectiveness in pretreating high-strength lignocellulosic biomass hydrolytes. For example, using a single-chamber air-cathode MFC with non-catalyzed electrodes, Mohan et al. [115] removed 63% of the high influent COD (52 g/L) derived from the hydrolyte of composite vegetables. At the same time, 57 mW/m² of electric power was able to be recovered. In another study, by integrating dark fermentation and single-chamber MECs, Li et al. [90] reported a considerable H₂ generation of 3.43 m³/m³/day with 44% of COD removed from the original 20 g/L of COD which resulted from corn stalk. These results showed that BESs can serve as potential pretreatment units for agricultural wastes and wastewater. Each type of BESs can be stacked for enhanced overall performance. In addition, MFCs can be used to supply the external electric power required for other BESs such as MECs and MESs [8], thus reducing the energy demand for waste and wastewater treatment while diversifying the added values from resource recovery.

Table 4. Performance comparisons of bioelectrochemical systems (BESs) for treating agricultural wastes/wastewater: MFC—microbial fuel cell; MEC—microbial electrosynthesis.

BES Type	Waste/Wastewater Type	Original COD (mg/L)	COD Removal (%)	Recovered Energy/Resources	Reference
MFC	Cattle manure slurry	2500	39	Electric power (163 mW/m ²)	[72]
MFC	Swine wastewater	8320	83	Electric power (261 mW/m ²)	[17]
MFC	Corn stover hydrolysate	1000	70	Electric power (867 mW/m ²)	[59]
MFC	Composite vegetables	52,000	63	Electric power (57 mW/m ²)	[115]
MFC	Starch processing wastewater	4852	98	Electric power (239 mW/m ²)	[116]
MEC	Swine wastewater	2000	75	Bio-H ₂ $(1.00 \text{ m}^3/\text{m}^3/\text{day})$	[92]
MEC	Corn stalk	20,000	44	Bio- H_2 (3.43 m ³ /m ³ /day)	[90]
MEC	Animal urine	1360	46	Bio-H ₂ (32.0 $m^3/m^3/day$)	[117]
MES	Lignocellulosic biomass	10,000	70	Butanol (0.88 g/L/day) Ethanol (1.99 g/L/day)	[118]

4.6. Water Desalination for Irrigation

Agricultural activities consume a great amount of water, accounting for approximately 70% of the total water usage globally [119]. At the same time, the continuing world human population expansion and deteriorating global warming have been adding more severity to the issue of water

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scarcity [120]. Although desalination technologies such as reverse osmosis, thermal desalination and electrodialysis have been maturely developed to supply high-quality freshwater in areas sufficient in brackish water and seawater but limited for freshwater sources, these technologies are energy-intensive and unsustainable [31]. MDCs are sustainable BESs specifically designed for low-cost desalination, which can overcome the drawbacks of the existing technologies and bring more economic, energy and environmental benefits to the desalination process [32]. Considering the low desalination rate using MDCs, most MDC systems today are applied for pre-desalination of seawater or desalination of brackish water (with less salinity than seawater) [32]. In many arid areas, freshwater shortage has forced farmers to use brackish groundwater for irrigation, which may temporarily relieve the freshwater stress but result in long-term issues such as accumulation of ions toxic to plants and increase of soil salinity [121]. High soil salinity can further weaken plants' ability to uptake water because of its resulting high osmotic potentials [121]. Therefore, in order to cause less harm to soil property and crop growth, the salinity of irrigation water should be ensured below 450 mg/L of total dissolved solids (TDS) [122].

Current MDCs have demonstrated solid abilities to desalinate brackish water to meet the standard of 450 mg TDS/L. For example, in a recent study using a continuously operated upflow MDC, more than 99% of NaCl in a salt solution that had a high salt concentration of 30 g TDS/L was removed at a significant desalination rate of 7.5 g TDS/L/day [123]. Ping et al. compared the desalination of three different types of brackish water at a hydraulic retention time (HRT) of 0.8 day and observed effective removal of salts and organic compounds [121]. As the HRT was increased to 1.7 days, the MDCs were capable of reducing TDS of brackish water to 110 mg/L, which was close to that of local tap water (i.e., 90 mg TDS/L) [121]. A predictive model for estimating salinity variation and individual ion concentrations in MDCs was also introduced in the same study for understanding the key factors in brackish water desalination in MDCs [121]. Other researchers investigated the effects of different low-cost catholyte solutions on MDC performance and observed sound desalination rates of 9.12 g TDS/L/day and 8.16 g TDS/L/day with bio-catholyte and buffer saline solution, respectively [124]. Moreover, larger-scale MDCs of 105 L were also tested for desalination of synthetic wastewater containing different concentrations of glucose, and considerable salt removal rate from 3.7 to 9.2 g TDS/L/day was observed [125]. Future research may aim to further scale up MDCs for stand-alone real-world applications with improved yields of freshwater. At the same time, MDCs can also be integrated with existing membrane-based reverse osmosis facilities to reduce energy demands during water desalination, which seems more promising in the near future until better system efficiency and durability of MDCs are upgraded [126].

4.7. Power Supply for Agricultural Monitoring Devices

In recent years, wireless sensor network (WSN) technologies that can automatically collect field information and perform real-time control of on-farm equipment have been actively developed and widely applied in agricultural practices to improve efficiency and automation in precision agriculture activities [127]. The agricultural monitoring devices such as remote sensors are typically powered by batteries or solar energy [127]. However, replacing batteries in remote areas is inconvenient and unsustainable, while using solar systems is inefficient, expensive and highly dependent on weather conditions [128]. BES technologies such as MSCs and EFCs have been extensively studied to provide sustainable power supply for WSN devices, with capacitors applied to accumulate excessive energy generated from these BESs [7,128–130]. Similarly, a specific genre of MFC known as sediment microbial fuel cell (SMFC) is widely used for powering wireless sensors and small telemetry systems to transmit the acquired data to remote receivers [131]. One of the first SMFCs was developed by Shantaram et al. over a decade ago by combining an MFC with low-power, high-efficiency electronic circuitry [132]. This early SMFC was already able to deliver a maximum voltage output of 2.1 V, which can be used to power most commercial electronic circuits (required at least 3.3 V) with the aid of a DC-DC converter to boost the potential [132]. For some SMFC applications (e.g., with substrates that are not

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readily biodegradable) that can only generate low potentials and recover electric power interruptedly, a power management system could be coupled to store and provide stable and continuous power to sensors [133]. The BES technologies can be specifically integrated with different agricultural sensor systems. Therefore, as the power source, diverse BESs can be used as power diverse wireless sensors for collecting climatological field data; acquiring irrigation management information; and monitoring the levels of plant nutrients, pesticides, pH, dissolved oxygen, conductivities, etc. in agricultural soils [134]. Further improvement of the electrode performance and system efficiency will make BESs a game-changing supplementary for WSN technologies in agriculture.

5. Potential Future Applications of BESs in Agriculture

5.1. Self-Powered Biosensors

BESs can not only power agricultural sensors, but also have the potential to be designed as self-powered biosensors that can be operated either in situ or online. Comparing with existing biosensors, depending on anolyte oxidations to provide external voltages, the current generated by BESs is directly related to the metabolic activities of the electrochemically active biofilm at the anode [135]. Changes of the metabolic activities in response to any disturbances are affecting the generated current in the circuit. If the operational conditions of BESs are controlled as constants, the rate change of electron generation can be translated into a signal that represents the magnitude of any specific disturbance [135]. Therefore, in a BES biosensor, the biofilm at the anode is the bioreceptor for recognizing the specific disturbance, while the transducer is the change of the electric current. For example, under unsaturated fuel conditions, a change in the organic substrate concentration (in COD) will lead to a direct change in the generated current, which makes the BES system a biosensor monitoring the biodegradable organics in the environment; under saturated fuel conditions, the BES system can be used to detect the level of inhibitors (e.g., toxicants) or stimulators, if all the other environmental factors are kept constant. In order to be used as biosensors, the BESs must demonstrate high sensitivity to the target compound near the anode. For BES biosensors, the sensitivity can be defined as the electric current change per unit analyte concentration change (normalized by the surface area of anode) [135]. Therefore, with the same change in anolyte concentration, a larger current change indicates higher sensitivity of the BES biosensor. When applied in real-world systems, BES biosensors can significantly cut down the maintenance expenses because there are no needs for external transducers and time-consuming immobilization of bioreceptors. The simplicity of design and operation also makes BES biosensors more advantageous over traditional chemical and biological sensors. However, the long-term stability of current output must be further improved for BES biosensors in order to generate more stable baseline signals [136]. Another technical barrier for BES sensors is to establish the predictive relationships between the signal responses and compound concentrations of different substrate chemicals [137]. To achieve this goal, more accurate mathematical models should be the tool to help our understanding. In addition, like for other BES applications, more high-performance but inexpensive materials should be developed for BES biosensors.

5.2. Growing Food Without Sunlight

Traditionally, sunlight is a necessity for plant growth. Plants need light to produce organic energy molecules such as adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) in the chlorophyll. These energy molecules carry high energy and electrons to the stroma for the fixation of carbon dioxide (CO₂) into carbohydrates via a reaction cycle known as Calvin-Benson Cycle [138]. In 2016, three researchers (Strik, D., van der Zwart, M. and Buisman, C.) in Wageningen University proposed the idea to produce food via anaerobic biosynthesis from wastewater and electricity [139]. In this study, energy and electrons generated in BESs would replace the role of ATP and NADPH produced in the first step of photosynthesis, while nutrients would be recovered from wastewater to support biomass growth. All can be accomplished in a self-sustaining closed system

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that efficiently utilizes the energy and nutrients recovered via circular pathways. The researchers named the process dark photosynthesis, which they believe can become practical in the near future to produce food in areas unsuitable for traditional agriculture [139]. Strik et al. estimated that a dark photosynthesis food reactor of approximately 1 m³ would be sufficient to provide food for three people [139]. This inspiring research shows the potentials of using BESs for alternative high-quality and sustainable food production approaches that are more energy- and water-efficient.

5.3. In-Situ Soil Remediation

Agricultural soils are vulnerable to different kinds of contamination, including acidification [140], petroleum hydrocarbon (mainly from on-farm vehicles) [141], metals [142], and transgenic toxins [143], etc. In order to reuse the contaminated soils for agricultural activities, in-situ remediation is required. Although BESs have been extensively studied for treating these contaminants in aqueous media, the effectiveness of BESs in soil remediation has been limited by the inefficient mass transport (e.g., O₂ and H⁺) in soils [144]. However, with appropriate methods to increase soil porosity and decrease Ohmic resistance, BES-based in-situ soil remediation can be a potent cost-effective tool in the near future. For example, using a two-chamber soil-MFC inoculated with activated sludge, Zheng et al. were able to ameliorate acidic soils from pH value of around 5 to nearly 6, while recovering electric current as high as 123.72 mA/m² [140]. Another research group succeeded in degrading 82.1–89.7% of petroleum hydrocarbon (originally 12.25 g/kg dry soil) within 120 days in a pilot study of column-type BESs that could be directly installed on site for in-situ soil remediation [141]. Nowadays, studies on BES-based soil remediation mainly use MFCs for electric power recovery because MFC technology is relatively more mature than other emerging BES technologies. However, with future breakthroughs in ion exchange and mass transport for soil applications of BESs, H₂ energy and other value-added chemicals can also be recovered on site along with in-situ soil remediation.

5.4. Reuse of Agricultural Wastes in BESs

While BESs can be directly used for different purposes in agriculture to provide economic, environmental and social benefits, agricultural wastes can also be converted into useful materials for lowering the high costs of BESs. Many lignocellulosic agricultural residues such as cotton stalk, rice husk, coconut coir, grass, vegetable fibers can be processed to manufacture construction materials [145], which can be used to build scaled-up BESs for sustainable energy/resource recovery. In addition, almost all types of agricultural biomass (including animal wastes) could be pyrolyzed to produce biochar, a novel soil amendment that can significantly improve the nutrient and water retention in agricultural soils [4]. Recent research has also explored biochar's potential for contamination treatment [146]. The pyrolysis process to produce biochar is often conducted under oxygen-limiting or oxygen-absent conditions at 300-700 °C, and the resulting biochar is usually characterized with a large specific surface area and good thermal stability [147]. Hence, the possibility to use highly porous electron-conductive biochar materials as the electrodes or electrocatalysts in BESs has been recently investigated [148–150]. Huggins et al. [148] used biochar electrodes made from forestry residue and compressed milling residue respectively to construct MFCs and observed considerable power outputs of 532 and 457 mW/m², which were comparable with those generated from MFCs using granular activated carbon (674 mW/m²) and graphite granule (566 mW/m²) [148]. According to an economic analysis, the power output cost of biochar electrode MFCs ranged from \$17/W to \$35/W, which is significantly lower (over 90%) than those of the MFCs using granular activated carbon (\$402/W) and graphite granule (\$392/W) [148]. Considering the great potential of biochar to act as relatively cheaper electrode materials, future studies should focus on investigating the suitability of more different types of biochar products for BES applications.

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6. Conclusions

Although different aspects of diverse BESs have been extensively studied, agriculture-driven BES research is limited despite its importance and significance in the face of the challenges relevant to food security, energy sustainability and freshwater availability. This review has updated recent agriculture-related BES studies and discussed the current and future BES applications in agricultural systems. Conclusively, BESs are sustainable technologies that can be integrated into agricultural systems for energy generation, resource recovery, waste minimization, wastewater treatment, irrigation water supply, and remote monitoring. It is also possible to design BESs as self-powered biosensors, as well as for food production and soil remediation. At the same time, agricultural wastes can also be utilized to construct scaled-up BESs or be pyrolyzed into biochar as lower-cost electrode materials. Long-term studies should be conducted in the future to assess the system stability and benefits of on-farm BES applications.

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