

*Review*

## Development of Bioelectrochemical Systems to Promote Sustainable Agriculture

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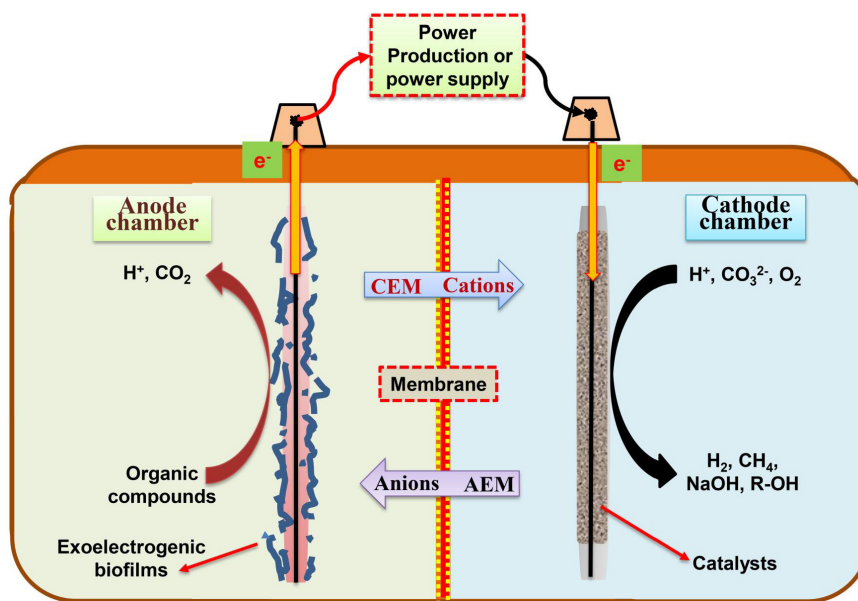
**Abstract:** Bioelectrochemical systems (BES) are a newly emerged technology for energy-efficient water and wastewater treatment. Much effort as well as significant progress has been made in advancing this technology towards practical applications treating various types of waste. However, BES application for agriculture has not been well explored. Herein, studies of BES related to agriculture are reviewed and the potential applications of BES for promoting sustainable agriculture are discussed. BES may be applied to treat the waste/wastewater from agricultural production, minimizing contaminants, producing bioenergy, and recovering useful nutrients. BES can also be used to supply irrigation water via desalinating brackish water or producing reclaimed water from wastewater. The energy generated in BES can be used as a power source for wireless sensors monitoring the key parameters for agricultural activities. The importance of BES to sustainable agriculture should be recognized, and future development of this technology should identify proper application niches with technological advancement.

**Keywords:** bioelectrochemical systems; microbial fuel cells; microbial desalination cells; anaerobic digestion; membrane filtration; wastewater reclamation and reuse; wireless sensors

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## 1. Introduction

Bioelectrochemical system (BES) has drawn great attention in recent years as an emerging technology for energy-efficient wastewater treatment, desalination, sustainable energy generation and value-added chemical production. In principle, BES takes advantage of microbial metabolism with electrodes to generate electricity via extracellular electron transfer (EET) [1] (Figure 1). Exoelectrogens (electrochemically active microorganisms) involved are capable of directly or indirectly transferring electrons to/from electrodes [2], referred to as electrode respiration [3]. Bacterial dissimilatory metal reduction (BDMR) has been regarded as the process closest to electrode respiration [2], with the *Geobacter* and *Shewanella* species identified as the most common BDMR model bacteria used in BES [4]. Development of BES can be classified into the following categories based on their application purposes: microbial fuel cells (MFC) [5], microbial electrolysis cells (MEC) [6], microbial desalination cells (MDC) [7], microbial electrosynthesis cells (MES) [8], *etc.* BES can be applied not only to treat the waste but also to harvest energy and value-added products. For example, electrical power [5] can be captured directly from the oxidation of organic compounds in MFCs while hydrogen [9] and methane [10] can be harvested from MECs.



**Figure 1.** A general schematic of bioelectrochemical systems (BES), CEM—cation exchange membrane, AEM—anion exchange membrane.

Among various forms of BES, MFCs are the most basic one, and extensive efforts have been made towards its development for practical application [11–13]. In MFCs, exoelectrogens have the capability of converting chemical energy to electrical energy. Electrons and protons are generated in an anode chamber during the oxidation of organic matters, and then transported through an external electric circuit to terminal electron acceptors (e.g., oxygen, nitrate, *etc.*) in a cathode chamber, incurring reduction reaction; cations such as protons are transferred to the cathode chamber via a separator (e.g., ion exchange membrane) or through the electrolyte. MFCs have the potential for energy efficient wastewater treatment, renewable energy production, water reuse and bioremediation [14]. The substrates used in

MFCs include a wide range of organic compounds including digested sludge, municipal sewage, landfill leachate, food wastewater, and marine sediments [15].

Water, energy and nutrient are the key elements for agricultural production that also generates a large amount of waste. The sustainability of agriculture is facing significant challenges [16,17], including an increasing demand for agricultural land and resources due to the rapid growth of population [18], environmental problems caused by excessive consumption of fossil fuels, fertilizers and pesticides, *etc.* Agricultural biomass, such as solid agricultural residues, and wet and dry manure, is considered as a renewable energy source because of its abundance and high organic content. BES appears to be of strong interest to address some of the key issues associated with water, energy and nutrient for sustainable agriculture. This review aims to introduce the past studies of BES related to agriculture, and discuss the critical factors essential for the development of BES for practical applications in sustainable agriculture, including treating agro-industrial waste, providing reclaimed water from saline water and wastewater, and powering the wireless sensors for agricultural monitoring.

## 2. BES for Agricultural Waste Management

BES can utilize a wide range of substrates produced from agricultural activities, generating renewable energy (electricity) with simultaneously degrading waste. Previous studies have shown that BES can perform either as a standalone process or as a post-treatment process for treating various types of agricultural waste.

### 2.1. BES as a Standalone Technology

#### 2.1.1. Animal Waste

Modern livestock agriculture has dramatically increased manure production. Application of manure as fertilizer and soil amendment can result in significant air and water pollution. For example, pollutants such as heavy metals, pathogens, hormones, and antibiotics in agricultural runoff can impair water quality [19]. The emissions of odor, methane, ammonia, and nitrous oxide can also affect air quality [20]. Therefore, animal waste should be treated appropriately to reduce its environmental impact.

Agricultural manure from animal confinements is rich in organic matters, and thus may act as a source of substrate for energy recovery using BES. However, based on the estimate of energy yield per unit mass of feedstock ( $\sim 10 \text{ kJ}\cdot\text{kg}^{-1}$  wet manure), manure may have a limited potential for electricity generation via MFC, mostly because of low conversion efficiency and complex substrate composition [21]. Table 1 presents a summary of energy recovery from animal waste in MFCs. In general, the power densities reported in the previous studies are highly diverse, ranging from several milliwatts to several hundred milliwatts per electrode surface area. The power density is largely affected by the substrates, MFC configurations and size [22,23], electrode materials, as well as operating conditions. Cattle manure as a representative of livestock was examined in two different MFC configurations, including a single compartment combined membrane-electrodes (SCME) and a twin compartment brush-type anode electrodes (TBE) without a proton exchange membrane (PEM) [24]. The electricity was produced at the rate of  $9.2 \text{ mW}\cdot\text{kg}^{-1}$  of dry manure in the SCME and  $24.3 \text{ mW}\cdot\text{kg}^{-1}$  in the TBE, suggesting that the brush-type anode design was more efficient than the conventional plate type electrode, probably due to

a larger surface area of the electrode. Factors such as moisture content, phosphate buffer solution (PBS), catalyst loading, and electrode area were investigated in a single-chamber, air-cathode MFC fed with cow manure, which showed that a higher moisture content was more suitable for current generation: moisture contents of 80%, 70% and 60% resulted in the maximum power densities of  $349 \pm 39$ ,  $36 \pm 9$  and  $12 \pm 2 \text{ mW}\cdot\text{m}^{-2}$ , respectively [25]. An MFC removed about 84% of BOD (biochemical oxygen demand) from cow slurry, while most of the nitrogen, phosphorus, and potassium were retained (84%, 70%, and 91%, respectively); the maximum power output was only  $0.34 \text{ mW}\cdot\text{m}^{-2}$  probably resulting from the presence of abundant inorganic matter, cellulose and lignin in manure [26].

**Table 1.** Performance comparison of microbial fuel cells (MFCs) for treating agricultural manure and wastewater.

MFC Type	Feedstock	External Resistance	Max Area Power Density	Max Volume Power Density	Original COD	COD Removal	Ref.
		$\Omega$	$\text{mW}\cdot\text{m}^{-2}$	$\text{W}\cdot\text{m}^{-3}$	$\text{mg}\cdot\text{L}^{-1}$	%	
S-MFC	cattle manure	470	36.6	0.2	1000	-	[24]
T-MFC	cattle manure	470	67	0.3	1000	-	[24]
T-MFC	manure sludge	-	5	-	-	-	[27]
S-MFC	Cow manure	1000	349	-	-	-	[25]
S-MFC	dairy manure	1000	189	4.7	-	-	[28]
T-MFC	cow waste slurry	460	0.34	-	1010	84	[26]
S-MFC	swine wastewater	200	261	1.2	8320	90	[15]
T-MFC	swine wastewater	1000	45	-	8320	-	[15]
S-MFC	swine wastewater	1000	228	-	8270	84	[29]
S-MFC	swine wastewater	10	-	1.08	12980	$0.523 \text{ kg COD m}^{-3}\cdot\text{day}^{-1}$	[30]

S—single-chambered; T—two-chambered.

Swine wastewater is another major animal waste with high strength of organic contaminants, odor problem and pathogenic risk [21]. The studies of swine wastewater treated by MFCs are summarized in Table 1. Typically, swine wastewater was diluted (5–10 times) to prevent inhibition of ammonia on exoelectrogen activities [15,30,31]. An early study used two MFCs to simultaneously generate electricity and treat swine wastewater containing  $8320 \pm 190 \text{ mg}\cdot\text{L}^{-1}$  of soluble COD [15]. The maximum power density obtained in a two-chambered MFC was  $45 \text{ mW}\cdot\text{m}^{-2}$ , much lower than  $261 \text{ mW}\cdot\text{m}^{-2}$  in a single-chambered MFC [15]. However, the Coulombic efficiency (CE) was relatively low (8%) in the single-chambered MFC, which was probably due to the diffusion of oxygen into the anodic chamber. In addition, soluble COD removal was increased from 88%–92% when the wastewater was stirred, while CE decreased from 8%–5%. It was found that a maximum power density of  $1415.6 \text{ mW}\cdot\text{m}^{-3}$  could be achieved from swine wastewater at a current density of  $3258.5 \text{ mA}\cdot\text{m}^{-3}$  when using Pt coated graphite felt and CEM; meanwhile, the organic and nitrogen removal rates were  $0.523 \text{ kg COD m}^{-3}\cdot\text{day}^{-1}$  (total anode chamber) and  $0.194 \text{ kg}\cdot\text{N}\cdot\text{m}^{-3}\cdot\text{day}^{-1}$  (total cathode chamber), respectively [30]. In addition to electricity generation, hydrogen can also be produced in an MEC treating swine wastewater [32]. The overall hydrogen recovery was  $28\% \pm 6\%$  of the COD, and hydrogen gas

accounted for  $77\% \pm 11\%$  of total gas volume. In contrast, little hydrogen gas could be recovered by fermentation of the swine wastewater unless it was autoclaved.

Different types of animal waste are rich in nutrients and thus it is of interest to investigate nutrient removal/recovery in BES. An air-cathode single-chamber MFC was used to recover phosphorus in the form of struvite crystal, which precipitated on the surface of the cathode electrode; however, the recovery rate of phosphorus was only 27%, accounting for a small portion of total phosphorus removal (70%–82%) [33]. Ammonia removal was examined in both single- and two-chambered MFCs, and the results suggested that nitrogen losses in the air-cathode system were mainly caused by ammonia volatilization due to elevated pH near the cathode, while nitrogen losses in the two-chambered MFC were primarily due to ammonium ion diffusion through the CEM [34]. In addition, nitrification likely occurred when oxygen was available, as ammonia-oxidizing bacterium *Nitrosomonas europaea* was detected on the cathode electrode.

The results of these previous studies indicate that animal waste has some potential as a renewable feedstock to produce renewable energy by BES. The barriers that can interfere with electricity generation include toxicity of ammonia at high concentrations, volatile fatty acids, as well as methane production [35]. The applications of BES in treating animal waste will depend on many factors such as the cost of the materials, treatment efficiency, and the amount of energy gained and consumed.

### 2.1.2. Plant Waste

Plant waste generated from agricultural activities is conventionally disposed by landfilling, composting, and incineration, leading to environmental concerns such as greenhouse gas emissions. Plant waste such as cellulose and lignocellulose has been considered as a potential source for renewable energy due to their abundance [36]. For example, biotechnologies have been developed to convert cellulosic biomass to energy products, such as hydrogen and methane [37]. The disadvantages of those bioprocesses include the availability of cellulolytic enzymes, generation of toxic intermediates, disposal of by-products, and high cost of gas separation, purification and storage [38].

BES has been investigated for treating plant waste. However, due to the complex composition of plant waste, the studies about treatment of plant waste by BES are limited, and pretreatment of complex waste to simpler forms appears to be essential. Table 2 shows the performance of the MFCs using cellulose biomass as substrates. It was found that both cellulolytic and exoelectrogenic microorganisms would be required for electricity generation in BES, because no single strain has yet been capable of producing electricity directly from cellulose [39,40]. An early study reported indirect electricity generation from cellulose in an MFC, through *in situ* oxidation of hydrogen that was produced from the anaerobic degradation of cellulose by cellulolytic bacteria (*Clostridium cellulolyticum* and *Clostridium thermocellum*) [41]. A defined coculture of the cellulolytic fermenter *Clostridium cellulolyticum* and the electrochemically active *Geobacter sulfurreducens* was used to generate electricity in a two-chamber MFC fed with cellulose (soluble CMC and insoluble MN301) [42]. The results showed that the coculture achieved maximum power densities of  $143 \text{ mW} \cdot \text{m}^{-2}$  and  $59.2 \text{ mW} \cdot \text{m}^{-2}$  from  $1 \text{ g} \cdot \text{L}^{-1}$  CMC and MN301 cellulose, respectively, while neither pure culture alone could generate electricity from these cellulose sources. Electricity was also produced from cellulose-MFCs using mixed and pure cultures of *Nocardiopsis* sp. KNU and *Streptomyces enissocaesilis* KNU as cellulose-degrading bacteria

biocatalysts [43] and mixed cultures with the rumen microbiota containing both strict and facultative anaerobes [44,45]. The low power densities in the MFCs treating cellulose were attributed to the high internal resistance of the two-chamber MFCs related to low conversion rate (Table 2) [36]. Thus, reducing internal resistance of MFCs and developing proper inoculum could increase power density [36]. For example, with a pre-acclimated inoculum from an MEC, the maximum power densities achieved in single- and two-chamber MFCs were  $1070 \text{ mW}\cdot\text{m}^{-2}$  (cathode area) and  $880 \text{ mW}\cdot\text{m}^{-2}$ , respectively [36]. As an exception, Rezael *et al.* [39] demonstrated for the first time that electricity can be generated from cellulose in a U-tube MFC using a single bacterial strain (*Enterobacter cloacae*) without exogenous mediators, though a very low power density of  $4.9 \text{ mW}\cdot\text{m}^{-2}$  was obtained.

**Table 2.** Performance comparison of MFCs for treating cellulose biomass.

MFC Type	Substrate	Strains or Culture	Anode Material	Max. Power Density $\text{mW}\cdot\text{m}^{-2}$	COD Remo val %	Ref.
MFC	$3 \text{ g}\cdot\text{L}^{-1}$ D-0	<i>Clostridium cellulolyticum</i> & <i>Clostridium thermocellum</i>	Pt-PTFA	$130 \text{ A}\cdot\text{m}^{-3}$ *	-	[41]
T-MFC	$1 \text{ g}\cdot\text{L}^{-1}$ CMC	<i>Clostridium cellulolyticum</i> & <i>Geobacter sulfurreducens</i>	graphite plates	143	38	[42]
T-MFC	$1 \text{ g}\cdot\text{L}^{-1}$ MN301			59.2	27	
T-MFC	$7.5 \text{ g}\cdot\text{L}^{-1}$ Sigmacell 20	ruman	graphite plates	55		[45]
T-MFC	$1.5 \text{ g}\cdot\text{L}^{-1}$	cellulolytic & exoelectrogenic bacteria	carbon paper	880	50–70	[36]
S-MFC	Sigmacell 20		carbon paper	1070	50–70	
3-T-MFC	$1 \text{ g}\cdot\text{L}^{-1}$ rice straw powder	<i>Nocardioptis</i> sp. KNU & <i>Streptomyces enissocaesilis</i> KNU	carbon paper	490	-	[46]
U-tube MFC	cellulose	<i>Enterobacter cloacae</i>	carbon cloth	4.9	-	[39]

S—single-chambered; T—two-chambered; \* current density.

Because of the recalcitrant characteristics of cellulose, pre-treatment processes are necessary to convert cellulose to readily degradable carbohydrates as substrates for BES. Instead of cultivating cellulolytic microorganisms, cellulose hydrolysis can be achieved directly by cellulase, which refers to a group of enzymes involved in cellulose hydrolysis, including endoglucanase, cellobiohydrolase, and  $\beta$ -glucosidase [47]. One drawback of using cellulase is that the reaction can be inhibited by the accumulation of end products (e.g., cellobiose and glucose that can bind active sites or prevent access to substrates) [41,48,49]. Cellulose hydrolysis together with other processes (e.g., fermentation) that simultaneously consume the hydrolysis products will help to address the problem [50]. For example, the combined cellulase of *Novozyme* 188 ( $\beta$ -glucosidase) and *Celluclast* 1.5 L was introduced to increase the power density from  $12 \pm 0.6 \text{ mW}\cdot\text{m}^{-2}$  in the absence of the enzymes to  $100 \pm 7 \text{ mW}\cdot\text{m}^{-2}$ , suggesting that cellulase and exoelectrogens have synergy [40].

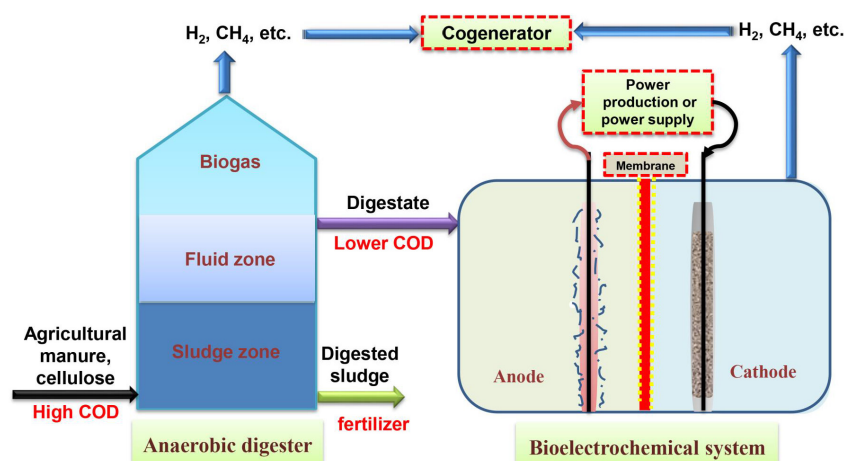
In addition to electricity generation, hydrogen gas can also be produced from cellulose in MECs [51,52]. For example, a fermentation-MEC integrated process was used to convert lignocellulose into hydrogen gas [51]. The inoculum of the MEC came from multiple MFCs pre-acclimated to a single substrate,

resulting in an improvement in the hydrogen yield and gas production rate. Hydrogen gas production from cellulose was also studied in an integrated system combining dark fermentation and an MFC as a power source for an MEC [52]. A hydrogen production rate of  $0.24 \text{ m}^3 \cdot \text{H}_2 \cdot \text{m}^{-3} \cdot \text{day}^{-1}$  was achieved at an overall energy recovery efficiency of 23% (based on cellulose removed) [52].

The above studies have demonstrated the technical feasibility of utilizing cellulose for electricity generation or hydrogen production in BES. In general, the power densities produced directly from cellulose are lower than those obtained from soluble substrates, and successful power generation requires specialized cultures and bespoke MFC configuration [36]. With an acclimated culture, reduced cost of enzymes and optimized system design, MFCs and MECs have a potential to be applied to take advantage of those abundant plant wastes from agriculture.

## 2.2. BES as a Supplementary Technology

For over a century, anaerobic digestion (AD) has been widely used for energy recovery (e.g., methane, ethanol and/or hydrogen) from solid and liquid waste. It has several exceptional advantages including remarkable bioconversion efficiency, low operating costs, and decreased sludge disposal expenses [14,53]. Both AD and MFC are capable of simultaneously treating organic waste and extracting energy from these sources using selected microbial communities [54]. AD systems typically receive a high strength influent ( $\geq 1000 \text{ mg COD L}^{-1}$ ), while BES allows to operate at low COD concentrations ( $\leq 1000 \text{ mg COD L}^{-1}$ ) [55], and perform as effluent polishing processes that convert residuals to electricity (MFC), hydrogen (MEC) or other products such as hydrogen peroxide [56] and caustic solution [57]. In addition, MFCs can directly generate electricity from organic waste without the need for gas purification, and they can perform at low temperatures ( $< 20 \text{ }^\circ\text{C}$ ) while AD does not perform well due to low reaction rates and high solubility of methane under such temperature [58]. Given the advantages and disadvantages of each technology, AD and BES may be integrated to achieve more efficient and thorough bioconversion of waste/wastewater [59]. As shown in Figure 2, MFCs may function as a post-treatment unit for AD, and such a combination could create synergistic effects by taking advantage of the benefits of each process. For example, a thermophilic AD has been coupled with MFCs to evaluate the stability of individual components when operating as a hybrid system [54], leading to an increase of overall energy production and more complete wastewater treatment.



**Figure 2.** BESs integrated with AD as a post-treatment technology.

BES can help recover nutrients such as ammonia from digester effluent. A high concentration of ammonia from manure and/or produced during the degradation of nitrogenous components (e.g., proteins, urea) will inhibit microorganisms involved in anaerobic digestion [60], thereby affecting the efficiency and stability of the process. Through integrating BES as a side treatment unit that recycles the digester liquid, ammonia can be recovered in either MFCs or MECs. In BES, to maintain charge neutrality, the flux of electrons caused by external power supply needs to be compensated by movement of cations. As a result, ammonium ions in an anode chamber will migrate through a CEM to a cathode [61], where it will be converted to ammonia gas due to the enhanced pH and then ammonia can be recovered by a stripping method. The recovery is affected by the operational parameters, such as current density, pH, ionic strength, and nitrogen concentration. It was showed in an electrochemical system (ES) that  $\text{NH}_4^+$  charge transfer efficiency and  $\text{NH}_4^+$  flux were achieved 96% and  $120 \text{ g N m}^{-2}\cdot\text{day}^{-1}$  at an energy input of  $5 \text{ kWh}\cdot\text{kg}^{-1} \text{ N removed}$ , respectively [62]. When being coupled with an upflow anaerobic sludge blanket (UASB) reactor to treat molasses, the ES can effectively control  $\text{NH}_3$  toxicity for digester and reduce  $\text{H}_2\text{S}$  emission, due to simultaneous  $\text{NH}_4^+$  extraction and oxidation of  $\text{H}_2\text{S}$  in the anode [63]. Oxidation of hydrogen sulfide has also been reported in BES studies [64–67]. BES in conjunction with anaerobic digestion would achieve similar effects as that of an ES; although BES may have lower performance due to low current generation, it does not require as much energy as the ES, thereby generating energy benefits. Recently, simultaneous ammonia recovery and electricity generation from ammonia-rich wastewater was demonstrated in a hybrid system consisting of a submersible MDC and a continuous stirred tank reactor, which could be applied to counteract ammonia inhibition during AD process [68,69].

A novel wastewater refinery concept has been proposed to recover more resources from waste streams but discharge less into environment [13]. In principle, wastewater with a low loading rate can be directly fed into an MFC, while the high-strength wastewater can be fermented in the AD system before flowing into the MFC system, for biogas production and for providing a suitable wastewater effluent [13]. The concept would also be applicable for treating agricultural waste, such as animal waste and cellulose biomass, achieving more efficient treatment and recovery of energy and other resources.

### 3. BES for Freshwater Supply to Agriculture

Water scarcity has severely affected the agriculture in most countries in the Middle East and North Africa, and many other areas in the world [70]. Agriculture is responsible for the primary water consumption in many regions of the world, accounting for 70% of the total global water demand [71]. In addition, the world population and associated demand for food are expected to increase significantly by 2050 [72]. Therefore, alternative sources of freshwater from seawater or brackish water desalination, and wastewater reclamation and reuse are becoming increasingly important in the future [73,74].

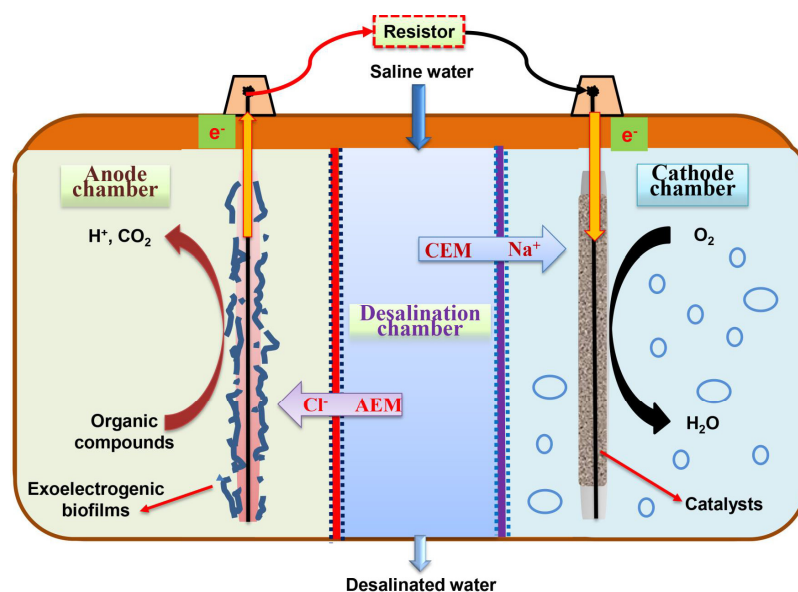
Desalination is an effective approach for producing high quality water, especially in those areas where brackish water and seawater are readily available but freshwater sources are limited [75]. The salt concentration of brackish water is between that of freshwater and seawater. Thus, brackish water desalination is promising as an alternative approach to increase the freshwater supply for drinking, irrigation and other purposes [76]. Mature desalination technologies such as thermal desalination, reverse osmosis (RO), and electrodialysis (ED) are typically energy-intensive and result in significant



operating costs, high water prices and potential environmental impacts [73,75,77]. Renewable energy sources such as solar and wind energy have been applied to drive the desalination systems but the capital and operating costs are still high [77]. These drawbacks associated with traditional desalination technologies have implied a need for developing new desalination technologies with economic, energy and environmental benefits [78].

### 3.1. MDCs for Saline Water Desalination

MDCs have gained great attention as a technology for sustainable wastewater treatment and low-cost desalination [79]. MDCs are derived from MFCs by placing AEM and CEM between anode and cathode, creating a middle chamber for water desalination [80] (Figure 3). To maintain electroneutrality, the electric potential gradient generated by exoelectrogenic bacteria drives cations and anions in the saline solution to migrate through CEM and AEM into the cathode chamber and anode chamber, respectively [81], thereby achieving desalination. The proof-of concept of MDC was firstly proposed by Cao *et al.* [7], and the technology has been advanced through both fundamental research and system development [7,82,83]. Because of the low desalination rate of MDC [84], two potential application niches have been identified. First, MDCs can be applied as a pre-desalination process, resulting in significant energy saving in downstream desalination processes [85]; and second, MDCs will be more suitable for desalinating brackish water rather than seawater, achieving a sound removal efficiency with shortened desalination time [78].

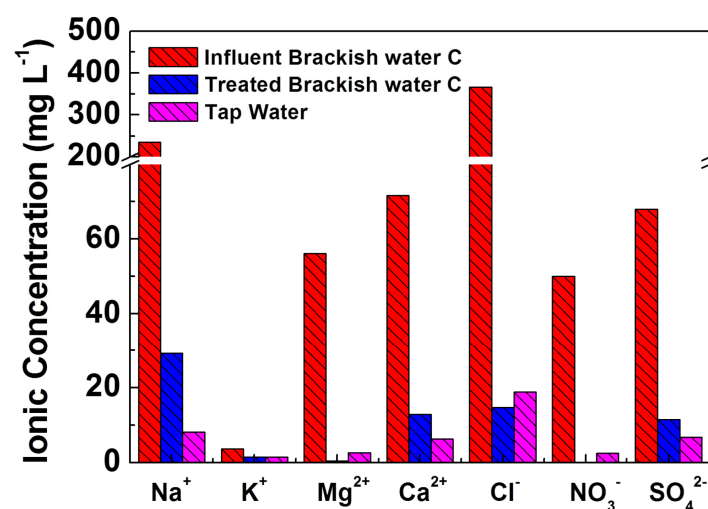


**Figure 3.** Schematic of a microbial desalination cell.

In many arid regions, brackish water is the main source of water supply [86]. Freshwater scarcity has forced farmers to irrigate crops with brackish water from shallow underground, which may relieve the drought crisis, but can cause the specific ion toxicity to plants and increase the risk of soil salinization [87]. For example, the salt content at different soil depths (upper 1 m soil layer) was significantly increased when brackish water with a salt content of 3.0–5.0 g·L<sup>-1</sup> was used for irrigation during the two growing seasons [87]. Consequently, high soil water salinity can further affect water uptake by crops due to high

osmotic potentials. The recommended salinity for irrigation water has been limited up to  $450 \text{ mg}\cdot\text{L}^{-1}$  of total dissolved solids (TDS) to reduce negative impacts on crops [88].

MDCs have the potential to desalinate brackish water and produce water that meets the irrigation requirement. This is demonstrated in a recent study, in which an MDC fed with three different types of brackish water achieved satisfactory desalination at a suitable hydraulic retention time (HRT) [86]. This MDC decreased the conductivity of the brackish water containing  $9.83 \text{ mS}\cdot\text{cm}^{-1}$  to  $0.41 \text{ mS}\cdot\text{cm}^{-1}$ , which met the non-restricted standard for agricultural use [86,89]. The concentration of  $\text{Na}^+$  in the desalinated water is a key parameter for assessing the irrigation suitability due to its strong influence on water infiltration and soil aeration [89]. The sodium adsorption ratio (SAR, the ratio of  $\text{Na}^+$  content relative to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  contents) has been used to evaluate the potential effects of sodium on crop growth and yield [90]. In the previously mentioned MDC desalination at a HRT of 1.7 d, SAR fell into the range of “slight to moderate restriction on use” for a brackish water sample (TDS =  $1.1 \text{ g}\cdot\text{L}^{-1}$ ) that had TDS reduced to  $110 \text{ mg}\cdot\text{L}^{-1}$ , slightly higher than that of the local tap water ( $90 \text{ mg}\cdot\text{L}^{-1}$  TDS) [86]. Furthermore, major ionic species were also effectively removed from this brackish water sample, with final concentrations at comparable levels to those in the tap water (Figure 4). These results have demonstrated that MDCs can reduce the salinity of brackish water by prolonging HRT and generate quality effluent for agricultural irrigation. Future research may focus on scale-up of MDCs and system optimization to further investigate their technical and economical feasibilities for practical application in agriculture.



**Figure 4.** Comparison of individual ion concentrations between the influent/treated brackish water and tap water sampled at Virginia Tech. Reproduced with permission from reference [86].

### 3.2. BES Integrated with Membrane Filtration for Wastewater Reclamations

Reclaimed wastewater has been widely applied for various purposes [74,91,92]. The application of reclaimed wastewater for agriculture irrigation is a common practice worldwide [93], because of the benefits such as conserving freshwater, saving fertilizers, and eliminating pollutants and nutrients discharging to water bodies [94,95]. However, long-term irrigation with reclaimed wastewater may lead to the changes of soil properties and accumulation of contaminants (e.g., organic matters, heavy metals),

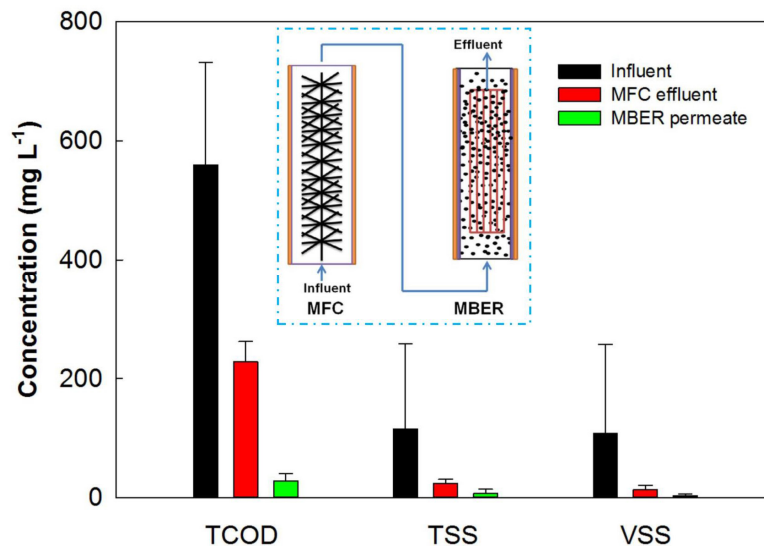
which consequently degrade soil quality and impact food safety [96]. Table 3 shows the reclaimed water quality criteria for agricultural irrigation regulated by U.S. EPA.

**Table 3.** Summary of U.S. EPA guidelines for water reuse for agricultural irrigation [97].

Agricultural Reuse Description	Treatment	Reclaimed Water Quality
<ul style="list-style-type: none"> <li>• Non-processed food crops</li> <li>• Any crop consumed raw by human</li> </ul>	Secondary Filtration Disinfection	<ul style="list-style-type: none"> <li>• pH = 6–9</li> <li>• <math>\leq 10 \text{ mg}\cdot\text{L}^{-1}</math> BOD</li> <li>• <math>\leq 2</math> NTU</li> <li>• No detectable fecal coliforms/100 mL</li> <li>• <math>\geq 1 \text{ mg}\cdot\text{L}^{-1}</math> residual chlorine *</li> </ul>
<ul style="list-style-type: none"> <li>• Processed food crops</li> <li>• Crops which are non-edible by humans, such as fodder, fiber, pasture, etc.</li> </ul>	Secondary Disinfection	<ul style="list-style-type: none"> <li>• pH = 6–9</li> <li>• <math>\leq 30 \text{ mg}\cdot\text{L}^{-1}</math> BOD</li> <li>• <math>\leq 30 \text{ mg}\cdot\text{L}^{-1}</math> TSS</li> <li>• <math>\leq 200</math> fecal coliforms/100 mL</li> <li>• <math>\geq 1 \text{ mg}\cdot\text{L}^{-1}</math> residual chlorine *</li> </ul>

\* A minimum contact time of 30 min.

To achieve a high quality effluent, various membrane separation processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), *etc.* are adopted in wastewater treatment and reuse, and they are able to eliminate suspended solids (SS), protozoa, bacteria, and even virus [98]. More information regarding membrane technologies for water supply in agriculture can be found in a recent review [99]. Among those membrane processes, membrane bioreactors (MBR) have been applied in wastewater treatment for reuse because of both biological treatment and physical separation, providing a consistent and high quality effluent for agricultural irrigation to save freshwater resources [99,100]. MBR technology can be integrated with BES to form a new system [101], for example a membrane bioelectrochemical reactor (MBER) can accomplish both direct electricity generation and membrane filtration [102]. To form an MBER, hollow-fiber membranes (HFM) were installed into the anode chamber of a tubular MFC, and membrane fouling was observed to be a key issue especially when operating at high organic loading rates and/or high water flux conditions [103]. To reduce fouling, a fluidized bed MBER was designed by adding granular activated carbon (GAC) in the anode chamber, which significantly reduced membrane fouling and achieved satisfactory removal efficiency of contaminants [104]. This MBER was coupled with an MFC for treating an actual industrial wastewater, showing an exceptional removal performance (Figure 5), and in this system, the MFC was observed as the major process responsible for contaminants removal and energy recovery, while the MBER functioned as post-treatment to obtain a high quality effluent [104]. HFM could also be installed in the cathode of an MBER alleviating membrane fouling by aeration [105]. This modified MBER achieved excellent COD and SS removal (90% and  $\sim 2$  NTU of turbidity, respectively), while total nitrogen removal was about 69% [105]. Disinfection process may be omitted because the bacteria are retained in the reactor by membranes. In addition, because the treated water is for crop irrigation, nutrients (N/P) do not need to be eliminated, and thus the remaining ammonium, nitrate and/or phosphate could be a valuable nutrient source for crops, which could reach an appropriate level to create a combined benefit of “fertigation” [106]. Therefore, BES integrated with membrane filtration could be an effective approach to supply freshwater for agriculture by wastewater reclamation.

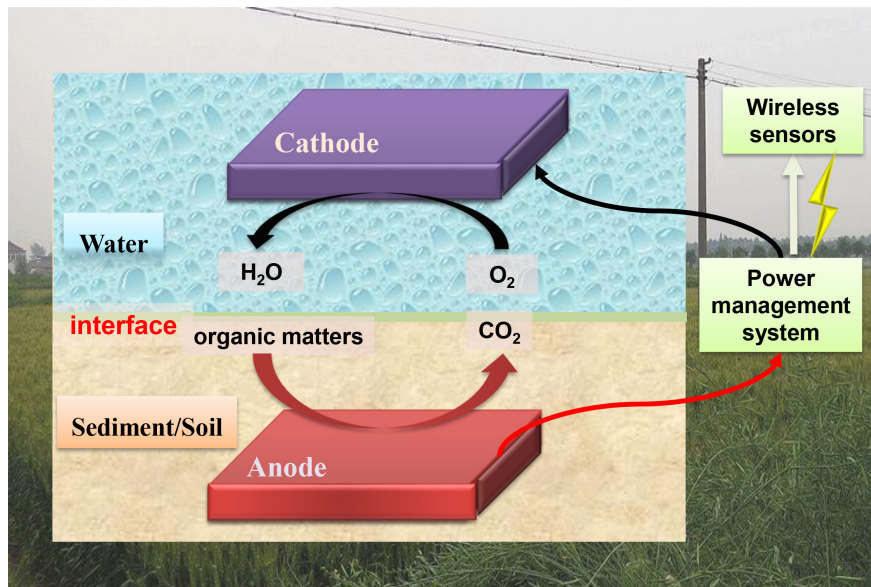


**Figure 5.** The contaminants removal from cheese wastewater by the coupled MFC–MBER system (see insert). TCOD: total COD; TSS: total suspended solids; VSS: volatile suspended solids. Reproduced with permission from reference [104].

#### 4. BES for Agricultural Monitoring

Wireless sensor network (WSN) represents an important technology used to achieve precision agriculture. WSN can detect and monitor spatial and temporal parameters for decision making in agricultural farm management [107–109], thereby increasing efficiency and productivity while minimizing undesirable impacts on environment [110]. WSN devices are mainly powered by either batteries or solar energy [111]. The potential drawbacks associated with these power sources make the sensors unreliable. For example, replacing batteries in a remote location can be very inconvenient and costly, while the solar system is more expensive and highly depends on weather conditions [112].

During the past decade, sediment MFCs (SMFCs) have been extensively studied for contaminant remediation and power generation [113–116]. SMFCs, consisting of an anode electrode embedded in sediment and a cathode electrode suspended in the water above the anode electrode, can extract bioenergy from aquatic sediments through bioelectrochemical reactions, similar to that in a regular MFC [116,117] (Figure 6). Unlike traditional MFCs, SMFCs do not require separators or ion exchange membranes because the oxygen gradient along the water column and sediment phases creates potential difference naturally (anaerobic/anoxic/aerobic zones) [117]. The electric power generated from SMFCs depends on the water and sediment conditions, the types of electrode material and cathode catalyst, and the distance between electrodes [117]. Dissolved oxygen (DO) is crucial for the cathodic reaction, and therefore SMFC is typically installed in shallow waters [118]. Previous studies have demonstrated that SMFCs can produce electricity and supply power to wireless sensors in both marine and fresh-water environments [113,119,120]. Capacitors have been adopted to accumulate energy generated from MFCs [121–124]. For examples, coupled with a power management system (PMS), electric energy extracted by SMFC was stored in ultracapacitors that consistently powered a remote sensor of 2.5 W deployed in the Palouse River, Pullman, WA, USA [125].



**Figure 6.** BES for powering wireless sensor for agricultural monitoring.

In precision agriculture, wireless sensors are deployed in fields to acquire micro-climatological data, such as temperature, humidity, sunlight, soil moisture content and wind speed, as well as to manage irrigation, fertilization, and pesticide [126–128]. The information obtained from sensors can help develop optimization strategies for crop production and save energy consumption, which is critical for achieving sustainable agriculture [129]. SMFCs may be served as an alternative power source for these wireless sensors, depending on their installation locations. They can be installed in wetlands, rivers or lakes near the farmland. To use the electricity, the output potentials must be boosted and operated by DC–DC converters and a PMS [119,120]. In the area where open water is not available, soil MFCs [130–133] or plant MFCs [134,135] may be applied. Essentially, they are analogous to SMFCs but oxidize organics in the soil under a low-moisture condition. In addition to the organics in soil/sediment, plants can also excrete organic matters as rhizodeposit, which can be utilized as substrates in MFCs [135]. For example, an MFC was installed in a rice paddy field during the rice-cropping season with graphite felt anode and cathode electrodes placed in the rice rhizosphere and the flooded water above the rhizosphere, respectively [136]. This study found that power generation from the MFC was sunlight dependent, and acetate (one of the major root-derived organic compounds) improved the electricity generation in the dark condition. A maximum power density of  $6 \text{ mW} \cdot \text{m}^{-2}$  (anode area) was achieved in this MFC, with the anode dominant species identified as a specific bacterial population of *Natronocella acetinitrilica*, *Beijerinckiaceae* bacterium and *Rhizobiales* bacterium [136].

In summary, BES might become an effective approach to power wireless sensors used in agriculture for various purposes, such as acquisition of micro-climatological data in the field, management of irrigation, fertilization, and pesticide, monitoring the parameters of agricultural runoff, such as pH, DO, turbidity, conductivity, nutrients (e.g.,  $\text{NO}_3^-$ ), etc. Further research is needed to improve power generation from two aspects, including the exploration of highly efficient electrodes and the optimization of system design. The choice of adopting SMFCs as a power source in agriculture monitoring will be highly case-specific due to many factors, including the accessibility of water sources, the water level, the

characteristics of sediment or soil (e.g., organic/moisture contents, permeability), the abundance and diversity of microorganism communities, and the availability of space for installation.

## 5. Conclusions

BES has great potential to be applied for promoting sustainable agriculture in the aspects of waste minimization, resource recovery, water supply, and agricultural monitoring. Despite a large amount of BES literature, the studies related to agriculture are limited. Thus, the interest in agriculture-driven BES research and development should be well recognized. Identification of proper application niches will be critical to BES development. Further studies should explore the BES performance with actual agricultural waste under non-laboratory conditions, system scaling up, and better assessment (e.g., LCA) of BES technology integrated with sustainable agriculture.

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## Conflicts of Interest

The authors declare no conflict of interest.

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