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Research review paper

Industrial bioelectrochemistry for waste valorization: State of the art and challenges

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ABSTRACT

Bioelectrochemistry has gained importance in recent years for some of its applications on waste valorization, such as wastewater treatment and carbon dioxide conversion, among others.

The aim of this review is to provide an updated overview of the applications of bioelectrochemical systems (BESs) for waste valorization in the industry, identifying current limitations and future perspectives of this technology. BESs are classified according to biorefinery concepts into three different categories: (i) waste to power, (ii) waste to fuel and (iii) waste to chemicals.

The main issues related to the scalability of bioelectrochemical systems are discussed, such as electrode construction, the addition of redox mediators and the design parameters of the cells. Among the existing BESs, microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) stand out as the more advanced technologies in terms of implementation and R&D investment. However, there has been little transfer of such achievements to enzymatic electrochemical systems. It is necessary that enzymatic systems learn from the knowledge reached with MFC and MEC to accelerate their development to achieve competitiveness in the short term.

1. Introduction

Bioelectrochemistry, which combined electrochemical and biochemical processes, has attracted much attention in the last ten years due to the contribution in terms of catalytic properties that biological agents (enzymes or living cells) can make to meet the sustainability and circular economy principles (de Fouchécour et al., 2022; Al-Sahari et al., 2021; Zhang et al., 2022; Chandrasekhar et al., 2021; Cai et al., 2022). The combination of biological systems with electrochemical cells is possible due to the fact that a key part of biological systems are involved in fundamental processes of energy use and capture (Barlett, 2008). For instance, redox reactions in microorganisms are involved in the oxidation of carbon substrates to CO_2 with the concomitant generation of energy molecules such as ATP; in the case of plants, solar energy is transformed into ATP molecules by means of cascade redox reactions. In both cases, there is a flow of electrons through an electron transport chain, which involves a series of redox proteins and enzymes in a constantly fluctuating state of oxidation and reduction. The application of an external voltage has been proven to yield to a certain degree of manipulation of cellular metabolism. For fundamentals, experimental techniques and applications of bioelectrochemistry systems see Barlett (2008).

Bioelectrochemical systems (BESs) have attracted much attention among researchers because they offer the advantage of combining the treatment of waste effluent with the simultaneous production of a valuable product (Zheng et al., 2020). BESs are able to harness the energy remaining in waste, which would otherwise be thrown away. Thus, BES technologies can be classified, according to the biorefinery concepts, in waste to power (WtP), waste to fuel (WtF) and waste to chemicals (WtC). WtP, WtF and WtC have become popular terms within the valorization of wastes, where the scope is to produce electric energy, fuels and organic compounds of commercial interest, respectively, by using waste as raw material.

In this context, wastewater, agro-industrial wastes and greenhouse gases, such as CO_2, are the main residues studied with BES technologies. Carbon dioxide is one of the main greenhouse gases, its anthropogenic generation being the main cause of the increase in concentration in the atmosphere. Carbon dioxide reduction is one of the major goals of the climate change battle and finding new alternatives is essential. Among the 17 sustainable development goals proposed by the United Nations, the capture and recycle of CO_2 is part of objective number 13: "Take

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Nomenclature

ABTS	2,2′-azino-bis(3-ethylbenzo- thazoline-6-sulphonc acid)
ADMI	American Dye Manufacturer's Institute
AEM	Anion exchange membrane
AC	Anodic chamber
AQDS	Anthraquinone-1,6-disulfonic acid
ATP	Adenosín trifosfato
BE	Benzoquinone
BeC	Bioelectrolytic cell
BES	Bioelectrochemical system
BesC	Bioelectrosynthesis cell
BFC	Biofuel cell
BOD	Biochemical oxygen demand
CC	Cathodic chamber
CE	Counter electrode
Ceff	Coulombic efficiency
CEM	Cation exchange membrane,
CO	Cobaltocene
COD	Chemical oxygen demand
DET	Direct electron transfer
E	Potential difference
EEC	Enzymatic electrochemical cell
EES	Electroenzymatic synthesis
EFC	Enzymatic fuel cell
f	Flow rate
FDH	Formate dehydrogenase
HRT	Hydraulic retention time
I	Current
i	Current density
IEM	Ion exchange menbrane
LCA	Life cycle assessment
MB	Methylene blue
MEC	Microbial electrolysis cell
MES	Microbial electrochemical synthesis
MET	Mediated electron transfer
MFC	Microbial fuel cell
MOF	Metal organic frameworks
MV	Methyl viologen
NA	Naphthoquinone
NAD^+	Nicotinamide adenine dinucleotide
NADH	Nicotinamide adenine dinucleotide (reduced form of NAD^+)
NER	Net energy recovery
NPV	Net present value
NR	Neutral red
OLR	Organic loading rate
Ox	Oxidized species
Pd	Power density
PEM	Polymer exchange membrane
PEMFC	Proton exchange membrane fuel cell
PHA	polyhydroxyalkanoate
PHB	poly (3-hydroxybutyrate)
PMS	Phenazine methosulfate
RE	Reference electrode
Re	Reynolds rotation number
Red	Reduced species
RI	Riboflavin
RM	Redox mediator
SHE	Standard hydrogen electrode
SPI	Specific power input
STS	Stirrer tip speed
TLR	Technology readiness levels
UASB	Upflow anaerobic sludge blanket.
V-Nase	Vanadium nitrogenase
VTR	Volumetric treatment rate
WAS	Waste activated sludge
WE	Working electrode
WIPO	World Intellectual property organization
WtC	Waste to chemical
WtF	Waste to fuel
WtP	Waste to power

urgent action to combat climate change and its impacts".

Around 380,000 million m^3/year of wastewater (equivalent to 152 million of Olympic swimming pools) are produced worldwide, and this value is expected to increase by ca. 2% annually (Qadir et al., 2020). Furthermore, according to a study performed by the European Commission, the treatment of wastewater that each individual produces leads to 17 kg/year of dry sludge (European Commission, 2017). Thus, it represents a huge problem for big cities due to the high volumes of wastewater that need to be treated and the high amounts of sludge that need to be discarded or processed annually. Some strategies for recovering bioactive compounds from sludge have been proposed (Cristina et al., 2020); however, they are not sufficient to considerably reduce the amount of waste that needs to be discarded. The current treatment of wastewater leads to a high energy expenditure, mainly related to the high requirements of aeration for the activated sludge process, which represents 50% of the energy requirement of the plant (Liu and Tay, 2001). The aerobic consortia require constant aeration since it is at this stage where most of the organic matter present in the wastewater stream is degraded. Paradoxically, the energy potential present in municipal wastewater ranges from 1.16 to 3.09 kWh/m^3 (Alsayed et al., 2020); thus, finding alternatives to recover this stored energy is crucial to meet the aspirations of a sustainable society.

In the last decade, an increasing number of scientific articles related to the development of BESs have been published, as shown in Fig. 1. The greatest number of publications are related to biofuel cells, and in particular, microbial fuel cells (MFC), which was the first BES proposed in the literature and is responsible to open opportunities for the development of novel applications of BES, like bioelectrolytic cells (BeC), and most recently bioelectrosynthesis cells (BesC), among others not considered in this review. Although efforts in the scientific community have been focused on the development of BESs for the conversion of wastewater and CO_2 into valuable products, their scalability to industrial level remains a challenge.

The first pilot-scale MFC system reported was a modular reactor with a volume of 1 m^3 using brewery wastewater as feedstock (Waller and Trabold, 2013). After almost a decade, there are a few companies offering MFC or MEC solutions for wastewater treatment (Jadhav et al., 2022). However, there is still no consensus in the literature about the criteria that need to be taken into consideration for the scale-up of BES reactors. This work aims to provide an updated overview of the applications of BESs for waste valorization in the industry to identify current limitations and future perspectives of the technology. In order to fulfill this objective, this review will be divided in four sections: 1. BESs, where the main parts involved in a bioelectrochemical cell and the mechanism of action will be described; 2. Bioelectrochemical approaches for waste valorization, discussing the wastes used as substrate and the respective commercially valuable products; 3. Consideration related to the scale-up of BES, where the main variables to take into account when scaling up BES to a commercial level will be described; 4. Projection of BES technologies; this final section will give a perspective of BES as a viable commercial alternative to apply in waste valorization.

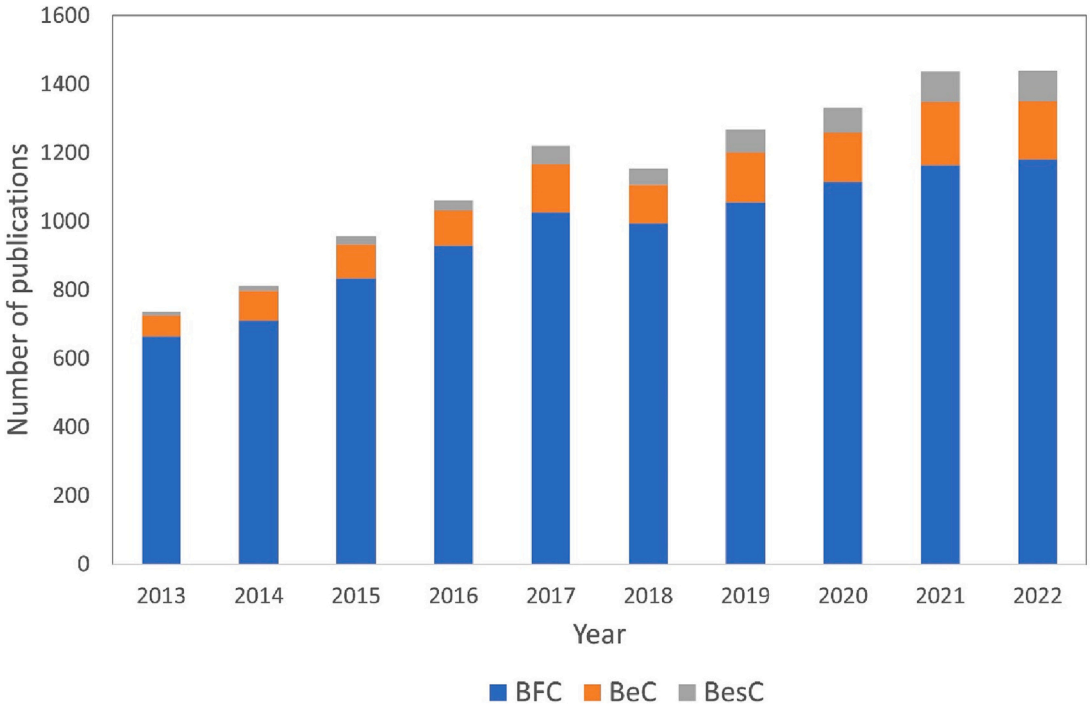


Fig. 1. Evolution of the number of scientific articles related to bioelectrochemical systems in the last decade, divided as biofuel cells (BFCs), bioelectrolytic cells (BeCs) and bioelectrosynthesys cells (BesC). (Source: Scopus, December 2022).

2. Bioelectrochemical systems (BESs)

BESs involve the use of microorganisms or enzymes with an electrochemical system to exert influence over the metabolism by affecting the oxidation and reduction ratios. BESs are unique systems capable of converting the chemical energy of organic matter into electricity, hydrogen or chemical products. In Fig. 2 a typical two-chamber bioelectrochemical cell configuration is depicted, with an ion exchange membrane in the middle as separator. At laboratory scale, the electrochemical cell is made up of a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). The reaction of interest takes place at the WE. The CE allows to close the circuit and the flowing of charges. RE serves for measuring the potential of a single chamber.

If the reaction is spontaneous in nature, the flow of electrons will allow the generation of energy; in this case, the electrochemical cell is a galvanic cell. If the reaction is not thermodynamically favorable, the energy needs to be applied from an external source to force the reaction; in this case, the cell is an electrolytic cell (Bajracharya et al., 2017).

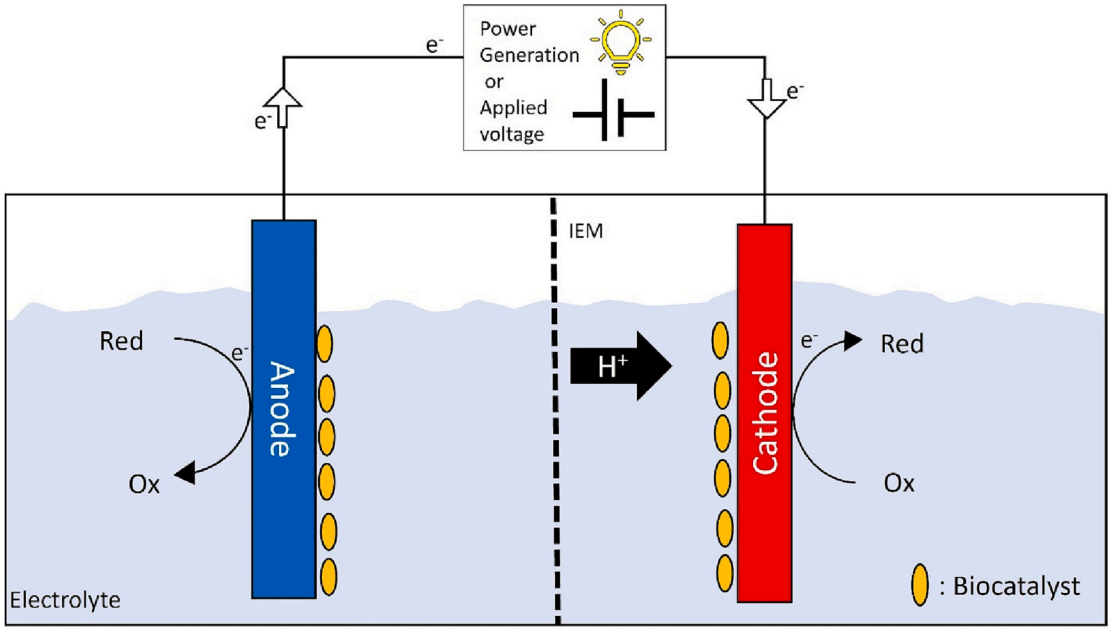
BESs make use of an electrochemical cell coupled to a biological catalyst to develop the reaction of interest, where the catalyst is either coupled to the cathodic or to the anodic chamber, depending on whether the reaction of interest is a reduction or an oxidation. In the case of wastewater treatment, the biological catalyst is located in the anodic chamber to oxidize the organic matter, as it occurs in microbial fuel cells (MFCs) or in microbial electrolysis cells (MECs). In the case of CO_2 conversion, the biological catalyst is located in the cathodic chamber in order to carry out its reduction (BesC).

Although most of the existing literature focuses on the use of microorganisms for the valorization of waste products, the use of enzymes has gained relevance in recent times (Cocuzza et al., 2022; Ottone et al., 2021a). The use of isolated enzymes presents clear-cut advantages to whole-cell systems, such as better control of reaction parameters and reaction monitoring, and avoidance of unwanted side reactions, leading to higher production yields (Petroll et al., 2019). Besides, the behavior in terms of reaction kinetics of the enzymatic BES is quite similar to chemical catalysts. However, in microbial systems the metabolic pathways and the synthesis of secondary metabolites need to be considered; however, crucial advances in protein engineering have allowed significant progress in enzyme biocatalysis and its implementation on an industrial scale of production for different products, even from non-conventional substrates (Sakkos et al., 2019).

In BES, electron transfer can be divided into two mechanisms: direct or mediated, as depicted in Fig. 3. In the direct electron transfer (DET) mechanism, the enzymes or microorganisms are directly wired to the electrode. In the case of enzymes, the DET of electrons occurs for distances between the electrode surface and the redox center of the enzyme below 1.4 nm (Kumar et al., 2017). The DET mechanism in microorganisms occurs when either the microorganism has conductive pili, or conductive materials/proteins are present in their outer membrane (Lovley, 2017; Mohan et al., 2014). As an example, *Geobacter* and *Shewanella* are electroactive bacteria in the group of microorganisms with reported DET capabilities (Creasey et al., 2018; Doyle and Marsili, 2018; Hirose et al., 2019; Lovley, 2011; Lovley and Walker, 2019).

The mediated electron transfer (MET) mechanism involves the use of redox mediators (RMs). RMs act as intermediate electron carriers between the biological agent and the electrode surface allowing to obtain the final redox reaction at the electrode surface. The possibility exists that the RMs do not establish a direct interaction with the catalyst to generate electron transfer, but interact with a third partner, such as a cofactor; this is called biological transfer of RMs and cofactor. A vast literature could be founded with respect to the use of redox mediators in the electrochemical regeneration of NADH (Gajdzik et al., 2012). Also, it has been observed that some microorganisms can secrete redox mediators; for example, a phenazine-based mediator has been found on MFC inoculated with *Pseudomonas* sp. (Pham et al., 2008).

RM are often used in BES to enhance the electron transfer from microorganisms or enzymes to the working electrode and can be of natural or artificial origin. Their uses in electrochemistry are based on their capacity to accept (reduce) and give (oxidize) electrons to other species (Martinez and Alvarez, 2018). A thorough discussion of redox mediators will be presented in the following sections.



	Anodic chamber		Cathodic chamber	
BES	**Red**	**Ox**	**Ox**	**Red**
Biofuel cell (BfC)	Organic matter	$CO_2 + H^+ + e^-$	O_2	H_2O
Bioelectrolytic cell (BeC)	Organic matter	$CO_2 + H^+ + e^-$	H^+	H_2
Bioelectrosynthesis cell (BesC)	H_2O	$O_2 + H^+ + e^-$	CO_2	Organic product

Fig. 2. Schematic representation of a bioelectrochemical cell applied for waste valorization with the production of energy, hydrogen or organic compounds. IEM: Ion-exchange membrane. The reduced (red) and oxidized species (ox) in each chamber will depend on the bioelectrochemical system (BES) as indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

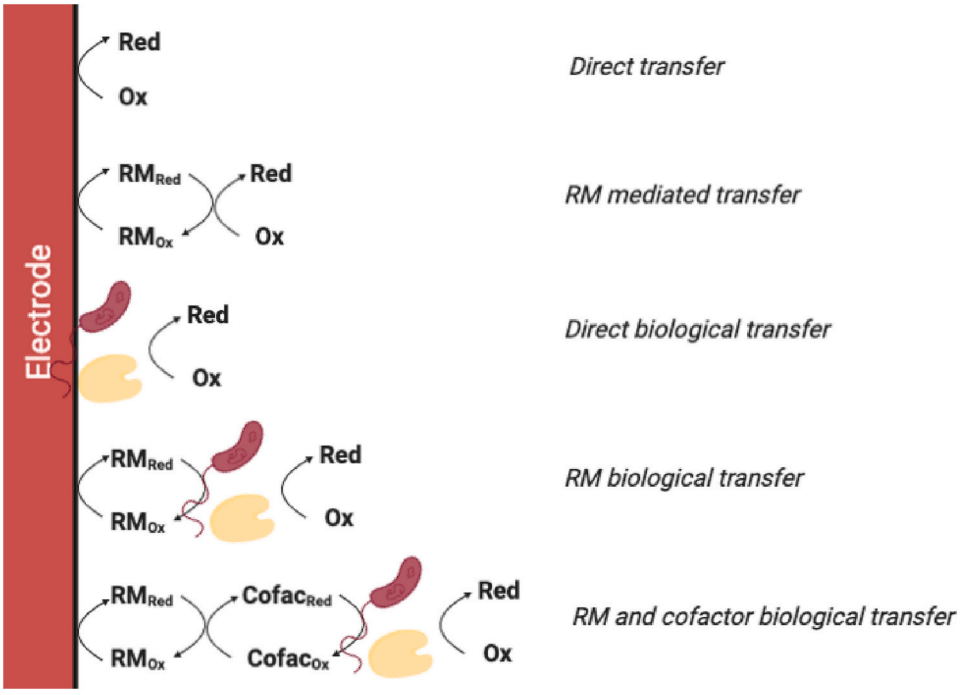


Fig. 3. Schematic representation of different mechanisms of electron transfer from electrode to redox species.

3. Bioelectrochemical approaches for waste valorization

This section gives a brief description of the different BES according to the classification of the biorefinery concepts WtP, WtF and WtC. A schematic diagram of the products and the systems involved is shown in Fig. 4.

In terms of the different substrates used in BES, the wastewater from agribusiness has great potential since it has a high organic load (chemical oxygen demand (COD) > 1 g/L) and a high degree of biodegradability (biochemical oxygen demand (BOD)/COD>60%) (Callegari et al., 2018). Therefore, these waste streams are highly attractive to be used in an MFC system. It should be noted that despite the development of current domestic wastewater treatment technologies, they are highly energy-demanding due to the need to stabilize this type of waste, so alternatives that allow energy reduction are extremely attractive.

3.1. Waste to Power with a biofuel cell (BfC)

The use of a biological agents, such as bacteria or enzymes, to produce energy in the form of electricity by means of an electrochemical cell is known as biofuel cells (BfCs). Microbial fuel cells (MFCs) are characterized by having the electroactive bacteria communities in the anode. The microorganisms consume the substrate from the media, growing and forming films on the electrode. Looking for further cell improvements, some researchers have proposed the use of biotic cathodes as well, as an alternative to overcome the limitation regarding oxygen as the ultimate electron acceptor. Among the different alternatives that have been proposed to reduce the overpotential, biocathodes have been highlighted as the most suitable for being cheap and easy to operate (Izadi et al., 2019; Mohamed et al., 2020; Samrat et al., 2018; Sindhuja et al., 2018).

In MFCs, an electric current flows through the anode chamber into the cathode chamber producing electricity by energy conversion from the breakdown of chemical bonds in the organic matter (Waller and Trabold, 2013). MFC cannot produce the same level of voltage and current density obtained in classical chemical fuel cells (Muddemann et al., 2019).

Analogous to MFC, enzymatic fuel cells (EFC) produce electric current by the catalytic oxidation of a fuel. Nevertheless, in contrast to MFC, the exploitation of waste as a substrate for EFC is still an emerging research field. Wastewater containing organic compounds could be potentially used as fuel for EFCs. For instance, alcohol dehydrogenase (Galindo-de-la-Rosa et al., 2018, 2020; Tomassetti et al., 2020) or glucose oxidase (Bahar and Yazici, 2018; Chung et al., 2018; del Torno-de Román et al., 2018) modified anodes have been studied using alcohol and glucose solutions, respectively. However, having waste valorization in mind, it is necessary to study the interactions that other molecules present in the waste may have with the electrochemical system. In addition, the high selectivity of enzymes works against the system, as they cannot efficiently utilize complex waste streams containing different organic compounds.

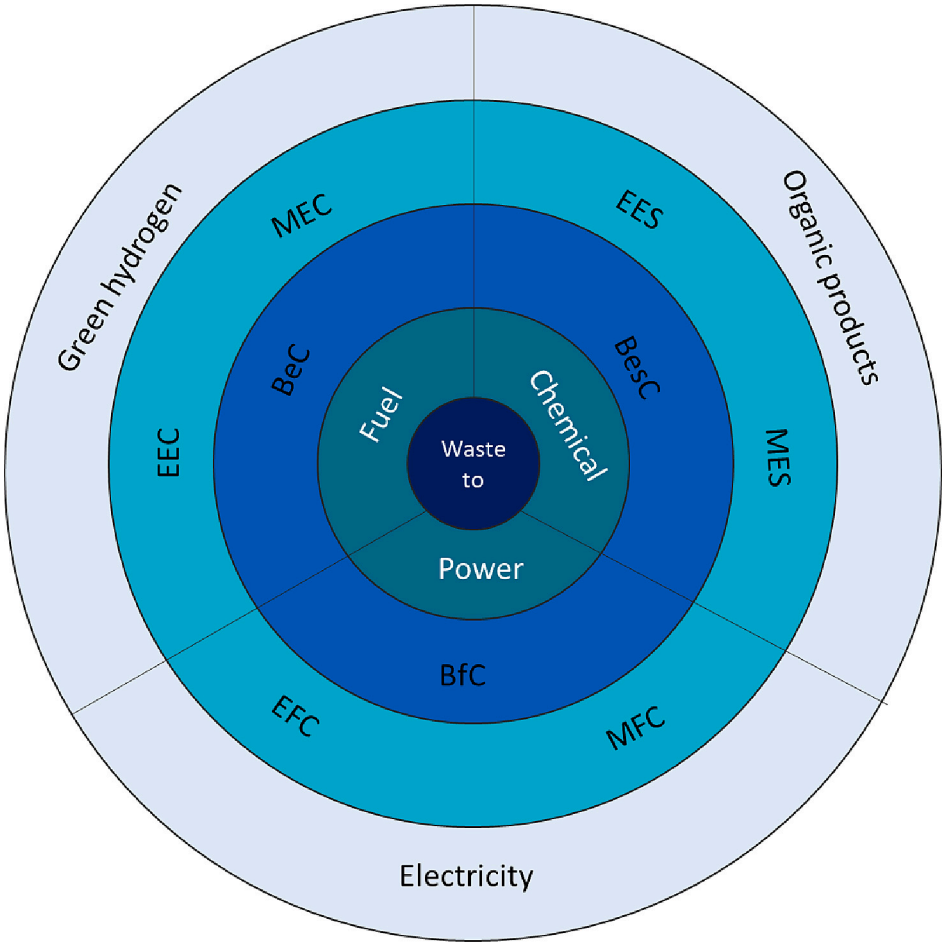


Fig. 4. Diagram of the products reported in the literature for the valorization of waste using a bioelectrochemical system technology. MEC: microbial electrolysis cell, EEC: enzymatic electrochemical cell, BeC: bioelectrolytic cell, EFC: enzymatic fuel cell, MFC: microbial fuel cell, BFC: biofuel cell, EES: electroenzymatic synthesis, MES: microbial electrochemical synthesis and BesC: bioelectrosynthesis cell.

3.2. Waste to Fuel with a bioelectrolytic cell (BeC)

Hydrogen (H_2) is recognized as one of the cleanest energy carriers, having a much higher gravimetric energy density than fossil fuels (Jia et al., 2020). So far, its production comes mainly from the use of fossil fuels (e.g Hydrocarbon catalytic reforming or coal gasification), which leads to huge emissions of CO_2 (Cormos et al., 2018).

An alternative environmentally-friendly technology for producing H_2 is the microbial electrolysis cell (MEC). While MFCs produce energy by organic matter oxidation, MEC requires an output source of energy to partially reverse the process to generate H_2 from organic matter (Chorbadzhiyska et al., 2011). H_2 is obtained at the cathode by the reduction of the protons produced by the degradation of organic matter at the anode (see Fig. 2). Usually, an ion exchange membrane separates the anodic and cathodic chambers allowing only the passage of protons. The use of the membrane has the advantage of producing H_2 with higher purity than obtained in the counterpart with only one chamber (Kadier et al., 2016). The voltage required for the reaction of H_2 production varies between 0.2 and 0.8 V, which is much lower than in a non-biological water electrolysis cell, which requires voltages between 1.23 and 1.8 V (Kadier et al., 2016). MECs have been used with a range of substrates similar to those already described for MFC, including wastewater. The organic matter removal from wastewater using MEC ranges between 60 and 90%, similar to that obtained with a MFC (Escapa et al., 2012; Hussain et al., 2018; Liu et al., 2012).

In an enzymatic electrolysis cell (EEC), hydrogenases containing the [Ni-Fe] and [Fe-Fe] groups can catalyze the hydrogen reaction in the cathode with similar oxidation rates than in a platinum electrode (Chenevier et al., 2013; Jones et al., 2002; Vignais et al., 2001). The differences between the two groups, [Ni-Fe] and [Fe-Fe], are the catalytic properties and the stability at aerobic conditions. The [Fe-Fe] group exhibits better catalytic properties than the [Ni-Fe] group (Bandyopadhyay et al., 2010), but the first one is strongly sensitive to oxygen (Lu and Koo, 2019). In general, [Ni-Fe]-hydrogenases are isolated from *Clostridium* and *Desulfovibrio* bacteria, as well as from some green algae, such as *Chlamydomonas* (Jugder et al., 2013).

3.3. Waste to Chemicals with a bioelectrosynthesis cell (BesC)

Waste to chemical represents the most complex option for chemical synthesis through bioelectrochemical conversion. Two large categories stand out in this field: the conversion of CO_2 to carbon compounds and the production of bioplastics from wastewater (Bajracharya et al., 2017). BESs offer a more sustainable alternative than traditional production methods, avoiding the use of fossil fuels, allowing the recycling of CO_2 and valorizing wastewater as raw material.

Most studies about MES have been focused on the production of methane (Cheng et al., 2009; Su et al., 2016) and acetate, where the latter represents more than 70% of all works reported in the last decade (Jourdin and Burdyny, 2021). Therefore, the involved mechanism is well-known and the effect of several operational conditions to increase productivity and efficiency has been reported. The productivity of acetate reported varies in a wide range between a few to some thousand g/day/m^3 depending on the culture type, strain origin, applied potential, electrode material, and cell configuration, among other main operational parameters (Hengsbach et al., 2022). Recently, the use of mixed cultures has attracted the attention of researchers because it allows to obtain chemicals with higher economic value than acetate, like middle-chain fatty acids (Tahir et al., 2021). However, there is no consensus in the scientific community about which strategy, whether mixed or pure culture, has more scalability opportunities since both have their pros and cons (Chu et al., 2021). Other products obtained by MES are biodegradable bioplastics, like polyhydroxyalkanoate (PHA) and poly (3-hydroxybutyrate) (PHB) (Dietrich et al., 2017). Nishio et al. (2013) reported that the production rate of PHB was increased by 60% when an electrically assisted system was used. The latter was attributed to an acceleration of the NAD^+/NADH redox cycle, which facilitates glycolytic metabolism and, in turn, PHB production. Other substrates, such as oily coffee waste, have been tested for PHB production by fermentation with *Ralstonia eutropha* (Bhatia et al., 2018), which illustrates the great potential of BES and the opportunities for waste treatment with the simultaneous production of valuable products.

Regarding the enzymatic reduction of CO_2, formate dehydrogenase (FDH) and vanadium nitrogenase (V-Nase) have been studied as catalysts for the one-step production of formic acid and methane, respectively (Kuk et al., 2019; Álvarez et al., 2017; Grasemann and Laurenczy, 2012; Su et al., 2016; Pietricola et al., 2020; Pietricola et al., 2021). Also, a cascade multienzyme system has been considered to produce methanol starting from CO_2 (Liu et al., 2020a; Ren et al., 2020; Zhang et al., 2021). In the reduction of CO_2 to formic acid with FDH, the nicotinamide dinucleotide (NAD) acts as RM, which is regenerated in the electrochemical cell (see Fig. 3). The regeneration of the cofactor is a key step for the integration of enzymes and electrochemistry, since its high cost makes regeneration mandatory for successful industrial implementation (Ottone et al., 2021b; Pietricola et al., 2022).

The electric wiring of nitrogenases differs from that the one for FDH since nitrogenases are ATP-depending enzymes. Although nitrogenases need ATP as a cofactor, the immobilization of the catalytic subunit of the enzyme on electrodes makes the cofactor dispensable with the consequent economic benefits making the use of nitrogenase-based systems more feasible for large-scale applications. Nitrogenase is made of two main components, a Fe-protein and a bimetal-protein ([Fe-V] or [Fe-Fe]). In the Fe-protein ATP is hydrolyzed to start the reduction cascade reaction which ends up on the [Fe-V] cofactor with the CO_2 reduction to CH_4 (Hu et al., 2018). In the EES systems, the coupling of the [Fe-V] or [Fe-Fe]-protein unit is done directly to the cathode, leading to a direct transfer of the electrons from the catalytic center of the enzyme to the cathode during the reaction of reduction of CO_2 to CH_4 (Milton and Minteer, 2019).

4. Considerations related to the scale-up of BES

BESs have shown great potential for waste recovery, but large-scale processes have not been developed yet. The need to study and identify the key variables in the scaling up of BES is fundamental; therefore, this section presents a compilation of different BES reported in the literature from laboratory to industrial implemented BES.

The highest TRL (Technology readiness level) value (TRL 9) was achieved with MFC, MEC and MES systems, whereas the highest TRL reported for the enzymatic system is TRL 3. On the other hand, to the best of the author's knowledge, no pilot-scale studies have been reported for any of the different enzymatic electrochemical systems. Fig. 5 shows a comparison between the number of total publications and patents reported for each BES technology. It can be inferred that there is a strong correlation between the highest TRL number achieved by a specific technology and the corresponding number of publications and patents.

It is worth noting that only a few commercially available products (TRL 9) have been reported for MFC (L.C.C. Aquacycl, n.d; Microorganic Technologies Inc, n.d; Plant-e, n.d), MEC (Electro-active Technologies Inc., n.d) and MES (Cambrian Innovation Inc, 2021). By searching in the Scopus database 'microbial fuel cell' AND 'scale-up', 92 articles were found whereas 28 articles were found by searching using 'microbial electrolysis cell' AND 'scale-up' as keywords.

Bird et al. (2022) defined some criteria for identifying when an MFC study can be considered to achieve the pilot-scale level, which can be extrapolated to the different BES technologies. The criteria consider reactor sizes higher than 10 L, the conduction of the reactor both inside and outside of the laboratory, the operation in either batch or continuous mode, operation times longer than one month and the treatment of any waste stream. Using these selection criteria, 30 pilot-scale MFC studies in the period between 2008 and 2020 were identified.

There is still little information regarding the TRL 9 BES, like

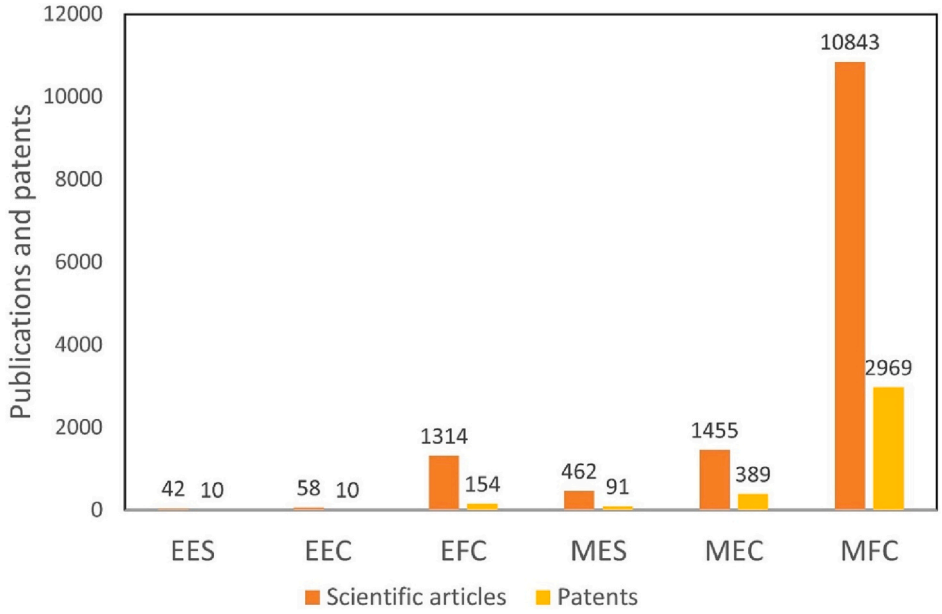


Fig. 5. Comparison between the number of publications and patents reported for the different BES technologies. Source: Scopus and WIPO, December 2022. EES: enzymatic electrosynthesis; EEC: enzymatic electrolysis cell; EFC: enzymatic fuel cell; MES: microbial electrosynthesis; MEC: microbial electrolysis cell; MFC: microbial fuel cell.

electrode material and reactor configuration, which is attributed to safeguarding intellectual property or the competitive edge of the companies. Therefore, to better understand the possibilities regarding the scale-up of a BES, the studies of TRL 4 and TRL 5 available in the literature will be used. Table 1 shows a summary of the different pilot-scale BES published in the last 5 years. In this selection, the only criteria taken into consideration was the size of the reactor (with a working volume bigger than 10 L). The working volume is the effective volume of the liquid inside the reactor, which considers the anolyte and catholyte (if present). The main characteristics of the cell construction like electrode material, reactor volume, separation of the anodic and cathodic chambers by means of a membrane as well as the type of microorganism used, waste treated, operational parameters and the performance of the different cells are indicated. It is interesting to note that more than 70% of the pilot-scale cells reported in Table 1 consider the use of a membrane for separating the anodic from the cathodic chamber even if one of the biggest issues related to microbial electrochemical cells is the membrane fouling. Nevertheless, the use of ceramic-based membranes, together with carbon-based electrodes highlights the necessity of finding novel cost-effective materials for the construction of the cells. In addition, ceramic materials have the advantage of being mechanically and chemically stable, which allows their regeneration by thermal or chemical treatments. COD removal efficiency and the power density values are typical parameters reported for comparing the performance of different MFCs. However, an important parameter that is hardly reported among the different pilot-scale prototypes is the Net Energy Recovery (NER), which indicates how much energy can be recovered from waste. Only the work published by Babanova et al. (2020) declares this result. This parameter serves as an indicator of how much energy can be used for other purposes different to waste treatment. NER is a useful parameter of comparison between an MFC and other WtP technology. In the case of MECs, there appears to be less consensus on the key parameters to assess performance. For instance, COD removal efficiency is not always reported and an important parameter like the COD to H_2 production yield is not calculated.

Other issues related to the scale-up of BESs are the electrode construction, the addition of a redox mediator, the configuration of the reactor and the downstream steps. These points will be discussed in detail below.

4.1. Construction of the electrodes

A fundamental component in any electrochemical systems, as well as in BESs, is the working electrode. The electrode is responsible for carrying out the reaction of interest, this being the cause of the various studies related to its optimization. Several variables are important for the construction and design of the electrodes, this being particularly relevant for large-scale applications, where size, surface area and cost considerations will determine the feasibility of BES.

As can be seen in Fig. 6, three are the key variables to be considered for the construction of the electrode: chemical composition, shape and morphology, and electrode's modification.

The chemical composition is directly related to the base material of the electrode and its chemical structure, giving the electrode its electrochemical characteristic and structural properties but, at the same time, directly influencing the type of interaction of the electrode with the biological catalyst. Shape and morphology are also critical parameters in the electrode design, where the required surface area and the desired final application must be taken into consideration. A third consideration is the possible modifications that can be done to the electrode to improve its properties, such as the increase in the surface area or in conductivity. Similarly to what occurs with other non-biological emerging electrochemical systems (Ottone et al., 2019), the reproducibility of the techniques for electrode construction at a large scale is one of the most important issues in scaling up.

As shown in Table 1, carbon-based materials, especially graphite-based, are the most used in scaling-up systems showing a good commercial perspective. Among them, graphite and its derivatives are the most attractive due to their relatively low cost, as shown in Table 2. The advantage of carbon-based materials relies on their lower cost per surface area, since carbon can be easily synthesized in a 3D structure like cloth, felt, and fiber among others. In this table, carbon granules and metal wools are not considered for their irregular shape that difficult the comparison with the same projected area. The data reported in Table 2 consider only the cost of the material used in the construction of the electride. It do not consider the cost of further electrode modifications like activation with functional groups nor thermal and chemical treatments of the base material.

Table 1
Specifications of pilot-scale BES published between 2018 and 2022.

BES	Waste	Working Volume (L)	Membrane	Anode material (projected area)	Cathode material (projected area)	Biological agent	Performance	Stable phase operation time (d)	Operational Parameters	REF
MFC	domestic wastewater	36	ceramic membrane (vermiculite)	graphite felt (0.756 m^2)	graphite felt air cathode (0.706 m^2)	anaerobic microbial consortium	COD removal: 93.52%, I: 43.7 mA, Pd: 23.52 $mW{\cdot}m^{-3}$, Ceff: 3%	92	fed-batch mode, HRT: 2–3 d	(Suransh et al., 2023)
MFC	dairy wastewater	0.855	CEM	graphite rod (0.003 m^2) with granular graphite bed (n.a.)	graphite rod (0.003 m^2) with granular graphite bed (n.a.)	activated sludge from the industrial plant treating the dairy waste samples	COD removal: 82%, Pd: 26.5 $W{\cdot}m^{-3}$, Ceff: 24%,	65	semi-continuous flow mode, f: 1 $L{\cdot}d^{-1}$	(Callegari et al., 2018)
MFC	domestic wastewater	850	no membrane	carbon fiber brush (11 m^2)	carbon air cathode (20 m^2)	effluent of previous bioelectrochemical systems *Fimbristylis ferruginea* with bacterial community from rhizospheric soils of plants	COD removal: 49%	100	continuous flow mode, HRT: 12 h, f: 5.76 $L{\cdot}min^{-1}{\cdot}m^{-2}$	(Rossi et al., 2022)
MFC	textile dye wastewater	30	CEM	316 stainless steel sheets (0.0126 m^2)	316 stainless steel sheets (0.0126 m^2)	growing at textile wastewater polluted site	COD removal: 74.1%, ADMI removal: 97.32%, Pd: 197.94 $mW{\cdot}m^{-2}$ (at 500 Ω)	4	batch mode, HRT: 2d	(Patel et al., 2021)
MFC	domestic wastewater	43.88	no membrane	graphite plate (0.848 m^2)	graphite plate (0.848 m^2)	macrophyte plants	COD removal: 81.67%, Pd: 24.104 $mW{\cdot}m^{-2}$, i: 23.844 $mA{\cdot}m^{-2}$	45	batch mode, cycle volume: 20 L, total cycles: 3	(Selvaraj and Velvizhi, 2023)
MFC	swine wastewater	110	no membrane	graphite fiber brushes (1.2 m^2)	gas diffusion cathodes (0.07 m^2)	lagoon sediment	COD removal: 65%, Ceff: 27%, i: 103 $mA{\cdot}m^{-2}$ (at 47 Ω), Pd: 92 $mW{\cdot}m^{-2}$, NER: 0.11 $kWhr{\cdot}kg^{-1}_{COD}$ (at 330 Ω)	170	continuous flow mode, HRT: 4 h, f: 660 $L{\cdot}d^{-1}$	(Babanova et al., 2020)
MFC	synthetic wastewater	125	ceramic membrane	graphite felt (0.027 m^2)	graphite felt coated with CuSn on air facing side (0.027 m^2)	plant secondary metabolites treated anaerobic sludge	Pd. 4.0 $mW{\cdot}m^{-2}$, Ceff: 5% (at 1 Ω), I: 40 mA (at 1 Ω)	160	continuous flow mode, f: 150 $mL{\cdot}min^{-1}$	(Nath and Ghangrekar, 2020)
UASB-MFC	synthetic textile wastewater	12.09	no membrane	graphite rod (0.022 m^2) with granular activated carbon bed (n.a.)	graphite rod (0.011 m^2)	secondary wastewater sludge from the distillery industry	Pd: 10.3 $W{\cdot}m^{-3}$, I: 285 mA (at 150 Ω), Ceff: 10.67% (at 150 Ω), COD removal: 71.73%	46	continuous flow mode, f: 0.72–1.2 $L{\cdot}h^{-1}$, HRT: 13.88 h	(Nakhate et al., 2019)
MEC	pig slurry liquid fraction	16	CEM	graphite felt (0.18 m^2)	graphite felt (0.18 m^2)	digestate from a local Wastewater Treatment Plant	H_2 production rate: 0.2 $LH_2{\cdot}L^{-1}{\cdot}d^{-1}$	5	fed-batch mode, cycle duration 2–5 d, f: 15 $L{\cdot}h^{-1}$, E: 1 V	(San-Martín et al., 2019)
MEC	domestic wastewater	45	ultra-high molecular weight polyethylene	graphite felt (1.44 m^2)	316 stainless steel flat mesh with stainless steel wire wool (0.6 m^2)	microorganism from the same wastewater	H_2 purity: 92.8%	100	continuous flow mode, HRT: 5 h, f: 150 $mL{\cdot}min^{-1}$, E: 0.9 V	(Verbeeck et al., 2018)
MEC	domestic wastewater	135	ultra-high molecular weight polyethylene	graphite felt (1.2 m^2) encased by two sheets of stainless steel mesh	438 grade 1 stainless steel wool (n.a.)	microorganism from the same wastewater	H_2 purity: 98.4%	100	continuous flow mode, HRT: 24 h, f: 75 $mL{\cdot}min^{-1}$, E: 1.2 V	(Verbeeck et al., 2018)
MEC	synthetic wastewater	12	AEM	granular graphite bed (n.a.)	granular graphite bed (n.a.)	activated sludge (anode), anaerobic sludge (cathode)	COD removal: 56%, I: 86 mA, Ceff: 13%	140	continuous flow mode, f: 6 $L{\cdot}d^{-1}$, HRT: 12.6 h, anode	(Zeppilli et al., 2020)

(*continued on next page*)

Table 1 (*continued*)

BES	Waste	Working Volume (L)	Membrane	Anode material (projected area)	Cathode material (projected area)	Biological agent	Performance	Stable phase operation time (d)	Operational Parameters	REF
MEC with denitrification	domestic wastewater	150	AEM	graphite felt (2.35 m2)	graphite felt (2.35 m^2)	activated sludge (anode), wastewater collected from the denitrification zone (cathode)	i: 0.27 $A{\cdot}m^{-2}$, Ceff: 10%, TOC removal: 80%, TN removal: 70%, specific energy consumption of 0.18 $kWh{\cdot}m{\cdot}L^{-3}$	63	potential: 0.2 V *vs.* SHE continuous flow mode, HRT: 1d, E: 1 V	(Maria et al., 2018)
MES	biowaste hydrolyzate (AC), CO_2 (CC)	12.5	AEM and CEM frame	316 L stainless steel frames with carbon tissue strips fixed between two stainless steel grills (0.36 m^2)	316 L stainless steel baskets filled with carbon granules (0.36 m^2)	electrode pieces from previous bioelectrochemical systems (anode). Fermentation licor of different food wastes (cathode)	COD removal rate (AC): 0.83 $g{\cdot}d^{-1}{\cdot}L^{-1}$, acetate production rate (CC): 0.53 $g{\cdot}d^{-1}{\cdot}L^{-1}$, acetate maximum concentration: 8.3 $g{\cdot}L^{-1}$, i: 2 $A{\cdot}m^{-2}$, Ceff: 98.6%	55	continuous flow mode (AC), f: 45 $mL{\cdot}d^{-1}$, E: 0.6–1.2 V, CO_2 flow rate (CC): ~ 1.5 $mL{\cdot}s^{-1}$, recirculation flow (CC): 100 $L{\cdot}h^{-1}$	(Tian et al., 2023)
MES	CO_2	50	CEM	graphite cloth (0.75 m^2)	graphite cloth (1.59 m^2)	*Methanococcus maripaludis*	Methane production rate: 11.7 $mmol{\cdot}d^{-1}$, i: 85 $mA{\cdot}m^{-2}$, Ceff: 100%	3.33	batch mode (liquid) with continuous gas flowing, HRT of gas: 33 min, E: −1100 mV *vs.* Ag/AgCl	(Enzmann and Holtmann, 2019)

Nomenclature: AC: anodic chamber, ADMI removal: American Dye Manufacturer's Institute removal efficiency, AEM: anion exchange membrane, BES: bioelectrochemical system, CC: cathodic chamber, Ceff: maximum coulombic efficiency, CEM: cation exchange membrane, COD removal: chemical oxygen demand removal efficiency, E: potential difference, f: flow rate, HRT: hydraulic retention time, I: highest current, i: highest current density, MEC: microbial electrolysis cell, MFC: microbial fuel cell, MES: microbial electrosynthesis, n.a.: not applicable, NER: net energy recovery, Pd: Highest power density, SHE: standard hydrogen electrode, UASB: upflow anaerobic sludge blanket.

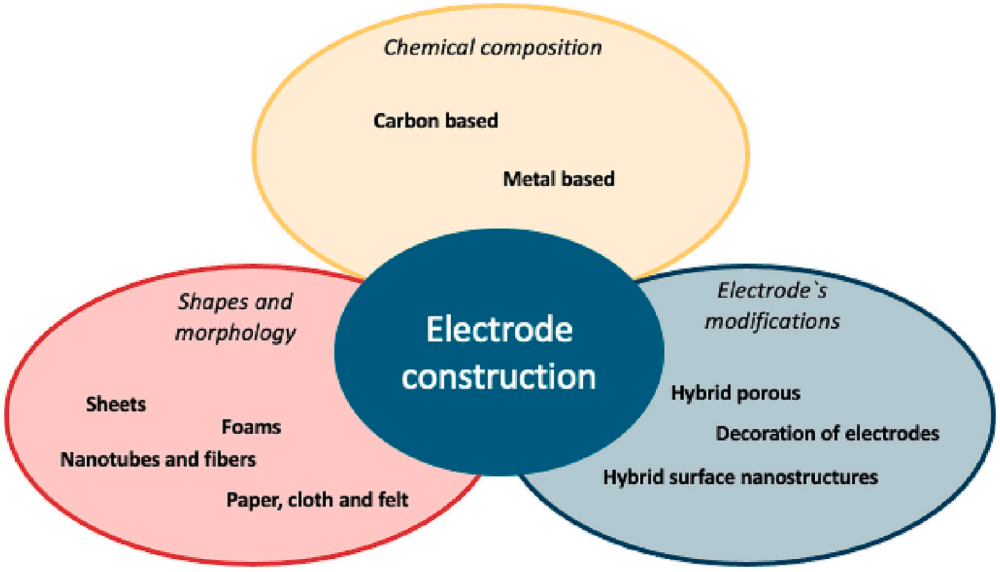


Fig. 6. Schematic representation of the key variables in electrode manufacturing.

Table 2
Comparison of the cost of different electrode configurations used in BESs considering 1 m^2 of projected area.

Electrode Dimensions	Material	Specification	Cost (Dólar) for 1 m^2 projected area	Total surface area (m^2)	Specific cost (USD/total area)	Source
3D		Cloth	1900	478	4,0	Fuel cell store
3D		Felt	856	66,3	12,9	Fuel cell store
2D	Graphite	Paper	469	1	468,8	Fuel cell store
						Sigma
2D		Plate	2110	1	2110,0	Aldrich
3D		Nanotubes[a]	9700	80,000	0,1	Sigma
	Graphene					Aldrich
						Sigma
2D		Paper	671	1	671,0	Aldrich
						Sigma
3D	Glassy carbon	Plate	3519	N.D.	N.D.	Aldrich
	Platinum					Sigma
2D	99.95%	Thin layer[b]	2854	1	2853,5	Aldrich
						Sigma
2D	Stainless steel	Sheet	1001	1	1000,8	Aldrich

[a] Considering a loading of 100 g of nanotubes per m^2.
[b] For a 100 nm deposited thin layer. The cost of the support material is not considered.

4.1.1. Chemical composition

The chemical composition is directly related to the materials used in the fabrication of the electrodes; here carbon and metal-based groups stand out. Among the family of carbon-based materials, graphite, graphene, and glassy carbon electrodes can be found. Carbon-based materials have some properties that make them attractive for electrochemical applications, such as good electrical conductivity and low resistance, high biocompatibility and chemical stability, resistance to corrosion, large surface area, appropriate mechanical strength and toughness (Dubey and Guruviah, 2019; Thamilselvan et al., 2016).

Metal-based electrodes have been widely studied also, and certain metals with good characteristics (conductivity, corrosion resistance, and chemical reactivity) for use in electrochemical cells are recognized. Some of the most used metals for electrochemical applications are copper, platinum, titanium and stainless steel (Terzi et al., 2019). Among them, stainless steel is an excellent material alternative for electrode manufacturing at large scale, with outstanding properties such as corrosion resistance, high electric conductivity and low cost compared to other metals. To increase the surface area, stainless steel foams have been proposed, showing robustness and biocompatibility to form biofilms for MFC applications (Kalathil et al., 2018).

Recently, new materials, such as metal organic frameworks (MOFs) and semiconductors (ZnO and TiO_2), have emerged with attractive electrochemical and mechanical properties (Ottone et al., 2014a, 2014b; Ottone et al., 2021b). However, these new materials are still under development for industrial use (Jaouen and Morozan, 2014; Liao et al., 2018; Vikrant et al., 2017), so they are not considered in this review.

Carbon and metal-based materials are the most used in the fabrication of electrodes, and the literature highlights some of their advantages such as the cost of production, high specific surface area and biocompatibility (Liu et al., 2020b; Ahn and Logan, 2010; Huong Le et al., 2017; Lin et al., 2019; Liu et al., 2004; Mohanakrishna et al., 2018; Rengaraj et al., 2011; Zhou et al., 2011).

Carbon-based electrodes are also attractive from a cost perspective, being significantly cheaper than metals widely used in electrochemistry, such as platinum and copper. This makes carbon-based electrodes extremely attractive for the construction of large-scale BES. Graphite-based electrodes are particularly suitable when considering the design of large-scale BES. Graphite-based electrodes do not need to be supported, can be easily subjected to bulk or surface modifications in order to improve their electrochemical and physical qualities, and are readily available from different commercial suppliers.

4.1.2. Shape and morphology

The shape and morphology of the electrode plays an important role in its construction. Based on the forms, they can be categorized as: sheets or plates, foams, nanotubes and fibers, materials based on cross linking or woven units. Different presentations have been developed to increase the specific surface area of the electrode, which is key to achieve better current densities and serve as catalyst support (Artsanti et al., 2017; Debe, 2011; Gude, 2016).

Sheets or plates are the usual and basic shape of electrodes, despite the low amounts of catalysts that can be loaded. This limitation is due to the low exposed area, as in MFC (Fu et al., 2012; Li et al., 2009; Zhao et al., 2009). The power densities observed for a MFC using a plate electrode were the lowest when compared to other electrode shapes, such as mesh or cylinder (Fu et al., 2012). The foam electrode structure presents a higher surface area compared with plane plate or sheet, resulting in an improvement on the electrochemical performance (Ali et al., 2014; Liu and Liang, 2000; Montillet et al., 1994; Sen et al., 2014). Among the different materials to be used, carbon-based foams have been recognized as exceptional due to their excellent properties, like high electrical conductivity (Degirmenci and Kirca, 2018; Wang et al., 2015).

Another of the most widely used forms reported in the literature are nanotubes and fibers, which can be used to build up more complex structures. Nanotubes and fibers are categorized in the same group despite their difference in size, which are about 0.4 nm and in the range of 5 to 10 μm of diameter, respectively (Bhatt and Goe, 2017; Peng et al., 2000). Nanotubes and fibers have been also carbon-based electrodes whose characteristics, like high mechanical strength and ductility, have been highlighted for electrode manufacturing. Moreover, excellent stability and conductivity have been attributed to carbon nanotubes (Zhou et al., 2011).

Lastly, materials formed from interlocking or woven units ca be found which are constructed in paper-like, cloth-like and felt-like shapes. Their structure is based on fibers or nanotubes, either interwoven (for cloth) or non-structured (for felt) (Huong Le et al., 2017; Kim et al., 2019), while in paper the fibers are held together in a resin matrix (Radhakrishnan and Haridoss, 2011). Developing a structure based on woven/ interlaced fibers or nanotubes has been found to improve the mechanical properties, in this way being possible to provide strength, stiffness and toughness to the electrodes (Dan-Mallam et al., 2015).

4.1.3. Electrode modifications

All the materials, shapes and structures described before can be modified to improve its electrochemical performance. These modifications have been classified as follows: hybrid porous, hybrid surface nanostructures and decoration of electrodes surfaces. The first class, hybrid porous, is based on those primary porous structures which are filled with another material with a high surface area; an example of this is the reticulated vitreous carbon foam, whose micro holes can be filled with nanofibers (Walsh et al., 2016). The second class, hybrid surface nanostructure, although defined as “tubes within tubes” is described as an arrangement of surface geometry with micropores filled with microtubes; an example of this technique is the use of nanotubular titanates which were incorporated inside the pores of a wide nanotube array by electrophoretic deposition (Bavykin et al., 2013). The last category is based on the deposition or decoration of nanoparticles on the electrode surface; this can be carried out by combining different techniques, such as redox gel for coating, electrochemical deposition and reduction of metal salts, among others. In the literature, this kind of modification is mainly focused on the deposition of metal on carbon-based materials (Dhibar and Das, 2014; Fattahi et al., 2011; Han et al., 2018; Jeromiyas et al., 2019; Quinn et al., 2005; Vaghari et al., 2016; Wang et al., 2007; Xia et al., 2015). More information regarding these modification techniques can be found in Walsh et al. (2016).

Carbon-based materials have the best relationship between physical properties, such as specific surface area, and electrochemical properties. The surface area available is extremely important because the material topography influences the bacterial adhesion to the surface or the biofilm formation, and it has been reported that bacteria preferably colonize porous, grooved and braided surfaces (Yuan et al., 2018; Flint et al., 2000; Whitehead and Verran, 2006). In reactions catalyzed by enzymes, the surface area of the electrode also plays an important role. The available surface area will determine the number of functional groups that can be added and, therefore, the enzyme load immobilized on the electrode (Camelin et al., 2022). An interesting review of some cases of different techniques for protein and enzyme coupling on electrodes has been recently published (Olloqui-Sariego et al., 2021).

As already mentioned, the most attractive materials for the construction of a bioelectrode are carbon and metal-based, but in terms of their ability to be modified, carbon-based electrodes have an advantage. This makes them extremely attractive to be used in the construction of electrodes for large-scale operation.

4.2. Addition of redox mediators

The selection of the BES arrangement will depend on the system to be mounted and the mediator to be used. The use of a free form of RM is recommended in cases where the mediator is cheap and environmentally benign. On the contrary, in those cases where the subsequent waste treatment is not efficient enough to eliminate the RM, their commercial value is high, or poorly soluble in the medium, immobilization will be required to achieve good results (Azhar et al., 2005; Motabar et al., 2021). Kochius et al. (2012) described in detail the immobilization techniques available for redox mediators.

RM can be used with different purposes depending on what is being targeted: increasing in pollutant removal efficiency or increasing in production efficiency. As an example, Sevda and Sreekrishnan (2012) observed that using RMs on MFC for the treatment of sewage and simultaneous generation of energy, a significant improvement on the removal of organic matter was obtained with the use of methylene blue or neutral red, but this good performance was not reflected in terms of energy production. Authors attributed this behavior to an alteration on the cellular metabolism caused by the RM at the level of perturbation in the $NADH/NAD^+$ ratio leading to an imbalance in cofactors which participate in many metabolic reactions (Ieropoulos et al., 2005).

Tamirat et al. (2020) highlighted some characteristics of RMs that should be met for its selection, such as high reversibility, fast kinetics, high solubility, and negligible side reactions. Table 3 presents a list of the most studied RMs that are compatible with microbial or enzymatic systems.

The studies regarding RM are focusing mostly on the kinetics of different redox mediators in conjunction with different substrates and the analysis of their response at the level of pollutant removal, power generation and/or production of products of interest. An example of the enhancing effect of some RM on BES is the effect of different concentrations of methylene blue (MB) over MFC systems where reported results show that the highest values of energy and electric current generated were observed with 0.3 mM (Rahimnejad et al., 2011) and 0.08 mM (Sevda and Sreekrishnan, 2012). These results highlight the peculiarity of each system and the need to optimize the addition of RM, in order to obtain the best possible results.

RM plays an important role in BES, and it can be applied in two formats: free form or immobilized on a support. Different studies have shown the use of free RM on BES, but this has a clear disadvantage because its recovery from the reaction solution is difficult or impossible with the corresponding environmental threat (Dai et al., 2016). Although the concentrations of RM used are in the order of μM or mM, the need for their continuous feeding makes them a heavy economic and environmental burden. To solve this, many studies use RMs in an immobilized form, thus, retention and reuse are favored. The use of RM has been shown to have a positive effect on BES, but the use in stoichiometric quantities is not feasible for the operation of continuous systems due to its high commercial price (Hollmann et al., 2006). It has

Table 3
Redox mediators and some of their characteristics.

Redox mediator	Redox potential (vs SHE)	Solubility in water*	Cost (USD/g)**	Form	Reference
Methylene blue (MB)	−0.1	43.6 g/L	3.12	Free/ immobilized	Thiele et al., 2008
Methyl viologen (MV)	−0.446, −0.760	620 g/L	49.8	Free	Aulenta et al., 2007
Neutral red (NR)	−0.325	50 g/L	41.7	Free	Harrington et al., 2015
Riboflavin (RI)	–	Poor	17.3	Free	Field and Brady, 2003
Cobaltocene (CO)	−1.88, −0.94 (vs SCE)	Poor (<1 g/L)	54.2	Immobilized	Zhao et al., 2015
Phenazine methosulfate (PMS)	+0.08	200 g/L	47.1	Free	Thiele et al., 2008
Anthraquinone-1,6-disulfonic acid (AQDS)	−0.184	–	–	Immobilized	Aulenta et al., 2010
Benzoquinone (BE)	+0.28	Poor	4.1	Immobilized	Hendler, 1977
Naphthoquinone (NA)	−0.145	Poor (3.5 g/L)	6.7	Immobilized	Meckstroth et al., 1981
2,2′-azino-bis(3-ethylbenzo- thazoline-6-sulphonc acid) (ABTS)	0.670	50 g/L	69	Free/ immobilized	Tsujimura et al., 2001

* Solubility defined at 25 °C and obtained from PubChem data base.
** Data obtained from SigmaAldrich catalogue.

been shown that the systems of RM removal are inefficient and it is known that, even at low concentrations, they can be environmentally hazardous (Azhar et al., 2005; Novotný et al., 2011). Therefore, the alternative of immobilizing RMs has become quite attractive and different immobilization strategies have been reported, such as adsorption, polymerization, entrapment and covalent linkage. More information at this respect can be found in Kochius et al. (2012).

4.3. Reactor configuration

The configuration of the electrochemical cell or reactor is also a key issue for the implementation of BES in a commercial application. Different configurations have been proposed, using one, two or three chambers. The main advantage of using one chamber relies on its simplicity; however, as all products are in a unique chamber, the downstream process become more complex. Therefore, the use of two chambers in which the anolyte and catholyte products are separated has been considered a preferable alternative. This two-chamber configuration allows for higher efficiencies since an ion exchange membrane is used to generate the two compartments, thus avoiding reverse reactions, minimizing side reactions and obtaining cathodic products of higher purity (Tiquia-Arashiro, 2020). However, one of the disadvantages of this configuration when using wastewater as a substrate is the membrane fouling (Hiegemann et al., 2019), i.e., due the accumulation of some of the particulate materials present in the waste stream (Hou et al., 2021).

The most prominent advances in reactor configuration have been in MFC systems, in which the plate-and-frame reactor proved to be a very convenient and versatile configuration. The plate and frame reactor, as shown in Fig. 7, presents a sandwich-style configuration, where the ion exchange plate and the electrodes are trapped between a series of plates and frames. With this type of configuration, scaling up the process is quite easy, by simply adding more modules to increase the cell volume (González-García et al., 2000). The main downside of this configuration is the poor or almost non-existent mixing and homogenization; to solve this, different alternatives have been studied, such as the management of the inlet flow and the use of flow dispensers in the middle of the reaction chambers (Arenas et al., 2020). In addition, an improved design is the inclusion of air cathodes which report positive effects comparing different MFC reactor configurations (Rossi and Logan, 2022). In air cathodes MFC, the oxygen in air can passively flows to the cathode through a hydrophobic layer without need of pumps and thus energy consumption.

In microbial fermentation processes, there are some criteria that permit the design of large-scale processes leading to the same productivity and product quality as that developed at a laboratory scale (Yang, 2010). Some of these criteria are geometric similarity, such as hydraulic retention time (HRT), specific power input (SPI), Reynolds rotation number (Re) and stirrer tip speed (STS). However, in the scale-up of bioelectrochemical reactors there is no consensus in the research community about which criteria should be taken into consideration.

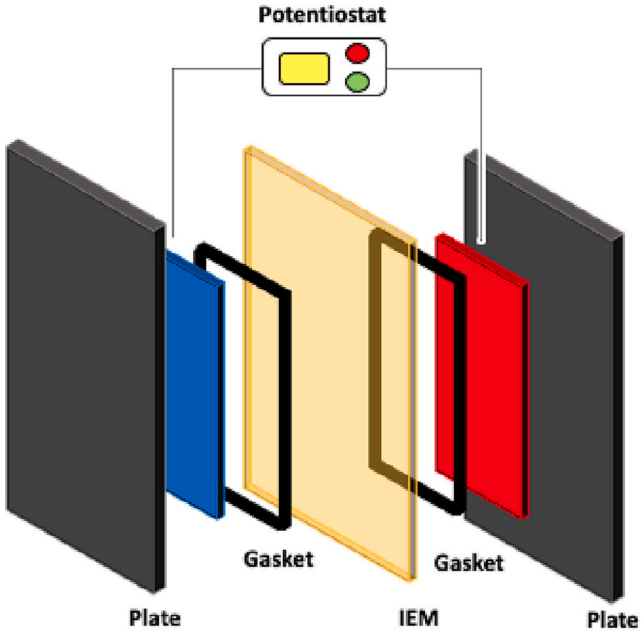


Fig. 7. Schematic representation of a plate and frame reactor. Blue and red electrodes represent the anode and cathode respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Considering that a large-scale BES will work in continuous mode and the relevance of maintaining the energy requirements, HRT and SPI have been considered for some scale-up BES reactors (Dekker et al., 2009; Fitschen et al., 2019; Haavisto et al., 2017; Walter et al., 2016; Ye et al., 2020). Other parameters proposed in the literature are specific current density, electrode spacing and electrode geometry (Cotterill et al., 2017; Jadhav et al., 2021; Janicek et al., 2014; Papillon et al., 2021). On the other hand, Reynolds rotation number or stirrer tip speed have been less proposed, since few MFC and MEC reactors have no agitation (Pan et al., 2019).

5. Challenges and future perspectives for BES technologies

Among the different BES technologies, MFC and MEC are the most developed systems with the greatest potential for commercial implementation in the near future. In particular, MFC technology is gaining significance for wastewater treatment because of its advantages with respect to the conventional technology of activated sludge which consumes much energy due to the requirement of constant aeration. However, certain aspects still require of improvements, such as reducing the cost of currently expensive electrode materials, proper wastewater pH control, and biofilm growth on the electrode's surface (Waller and Trabold, 2013). The intensification of the BES processes is a key strategy for achieving the commercialization level of the technology, analogous to what has been proposed for other biochemical processes (Boodhoo et al., 2022).

The differences between laboratory conditions and relevant environmental conditions need to be taken into consideration for reaching the market. The variation of substrate parameters, including temperature, pH, concentrations and components, is an important issue to have into consideration (Sulaymon and Abbar, 2012). Therefore, good design of pilot-scale experiences is necessary for giving useful information for offering attractive BES-based solutions. Interestingly, wastewater treatment in small rural communities, where throughputs and workloads are much lower, rises as a feasible option for introducing BES technology (Nagendranatha Reddy et al., 2018).

Another important parameter to consider in BES technology is COD removal efficiency. It was reported that the limit of COD removal with MFC is 1.1 kg COD/(m^3d), which represents between 60 and 70% of COD removal from the original affluent (de Fouchécour et al., 2022). On the other hand, traditional wastewater treatment (aerobic and anaerobic) leads to COD removal yields over 90% and, most importantly, it is possible to reach a final COD concentration below the disposal standards (Aziz et al., 2019), something that it is not possible to reach with current BES technologies. Each region has its own discharge standards; however, the limit of COD concentrations varies between 125 mg/L to 60 mg/L (Deng and Wheatley, 2016; EPA, 2001; E. U. W. Directive, 1991). Since BESs lead to lower COD removal yields than traditional wastewater treatment, it should be highlighted that the purpose of their implementation is to have a higher energy recovery and allow their coupling to another traditional treatment system to reach a COD value below the disposal regulation parameters. Related to COD removal, other reactor design parameters arise, like organic loading rate (OLR) and volumetric treatment rate (VTR), from which hydraulic retention time (HRT) can be obtained (Baeza et al., 2017). Thus, the requirements for waste treatment are a key factor in introducing BES technology as a competitive solution.

BES seems to be disadvantageous when compared to conventional technologies. For instance, the highest hydrogen production rate reported with a pilot-scale MEC using urban wastewater is 0.004 Nm^3/d (Baeza et al., 2017), which is considerably lower than obtained with a polymer exchange membrane (PEM) electrolyzer that arrives at 720 Nm^3/h (Dincer and Acar, 2015). In the case of MFC, the highest power density reported with a pilot-scale reactor is 60 W using a 1000 L reactor for treating municipal wastewater, which is still orders of magnitude lower than that produced with a proton exchange membrane fuel cell (PEMFC), which varies from 1 to 100 kW (Felseghi et al., 2019). Thus, with current materials used in the construction of the cells, the cost of using BES for wastewater treatment is still significantly higher than activated sludge or anaerobic digestion (Rozendal et al., 2008). According to a study performed by Christodoulou et al. (2017), formic acid is the product that can be produced by means of a MES with the lowest production cost (0.49 £/kg), which is a competitive cost with respect to traditional production systems. However, the current investment costs associated with MES are higher than that of conventional technologies, which represents the most important limitation for investors. A complete study of techno-economic analysis and sustainability through the life cycle assessment (LCA) methodology of different BESs is reported elsewhere (Savla et al., 2021). Thus, MFC and MEC are still far from being able to compete with ongoing technologies in high throughput wastewater treatment plants. However, a feasible option for this technology is wastewater treatment in small rural communities, where throughputs and workloads are much lower (Nagendranatha Reddy et al., 2018). Nevertheless, from an economic point of view, the revenues related to the treatment of the waste are a key factor to consider in the equation that could lead to a positive net present value (NPV) in a techno-economic analysis.

Moreover, it has been demonstrated that it is possible to use a MEC for the treatment of waste activated sludge (WAS) (Hu et al., 2019), which arises as a promising application of BESs because the accumulation of WAS is a big problem in traditional wastewater treatment plants (Lu et al., 2012). In addition, among the different biological strategies to produce hydrogen, MEC has been defined as the most promising technology due to its better control over hydrogen generation rate and effective conversion of organic feedstock, regardless of thermodynamic limits (Qyyum et al., 2022). The latter suggests that MEC technology will achieve a rapid advance toward maturity.

6. Conclusions

BES systems have been studied from different perspectives, such as biocatalyst components, electrochemical reactor configuration and electrode construction, among others. However, much more applied research is needed for its commercial application. Such efforts should be primarily focused on electrode manufacture optimization since it is one of the main factors affecting investment costs. For this reason, areas such as material for electrode construction and techniques of electrode modification to ensure a better biocatalyst attachment to the electrodes are critical to be further developed. Although different materials have been studied for electrode fabrication, the high production costs associated to the difficult scale-up of the synthesis procedures for electrode manufacture is a crucial issue that needs to be addressed to become a competitive technology.

Among the different BES, the microbial cells stand out as the most promising technology to expand their applications to reach technological significance in the short term because of their advances in technology implementation and R&D investment compared to the enzymatic technologies mentioned. It is necessary that the BES technologies that are in lower TRL values, such as enzymatic electrochemical cells, learn from the knowledge reached with the already commercially available technologies to accelerate their development and thus reach the competitive level in a short period of time.

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Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

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