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Bioelectrochemical cells as a green energy source for electrochemical treatment of water and wastewater

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Abstract

The quest for renewable energy sources to drive different sectors of the economy has become essential, owing to the continuous depletion of fossil fuels as well as environmental hazards associated with it. Bioelectrochemical cells (BEC), where microbial activities convert the energy stored in the form of carbon in waste to bioenergy, nutrient and value-added chemicals, is seen as an exciting alternative for simultaneous energy production and environmental remediation. BEC have been successively utilized for driving different electrochemical reactors applied in water/wastewater and contaminated soils remediations and nutrient/chemical recovery. This review concisely summarizes the principle, design and applications of BEC as a green energy source for electrochemical treatment of water and wastewater. The various BEC coupled energy systems, critical factors affecting the BEC performance, different BEC coupled electrochemical processes and challenges in scaling-up of coupled systems for long-term performance were critically discussed in this review.

Keywords: Bioelectrochemical cells (BEC); water and wastewater treatment; BEC coupled energy systems; and BEC coupled electrochemical processes

Highlights

- Energy produced from BEC is an affordable energy source for electrochemical processes
- The combined system is able to remove pollutants in a sustainable manner
- Both BEC and electrochemical systems are able to remove pollutants

Abbreviations:

ACF- Activated carbon fibers

AEM – Anion exchange membrane

ATP- Adenosine tri-phosphate

BEC – Bioelectrochemical cells

BET - Bioelectrochemical treatment

BPA - Bisphenol A

CDI- Capacitive deionization

CEM - Cation exchange membrane

CNTs - Carbon nanotubes

COD-Chemical oxygen demand

DC-Direct current

EAB - Electrochemically active bacteria

EC-Electrocoagulation

EES - Enzymatic electrochemical system

EF-Electro-Fenton

EO-electrooxidation (electrochemical oxidation)

GO-SPEEK - Graphene oxide self-fabricated sulfonated polyether ether ketone membrane

IEM - Ion exchange membrane

MDC - Microbial desalination cell

MEC - Microbial electrolysis cell

MES - Microbial electrochemical systems

MESC - Microbial electrosynthesis cell

MET - Microbial electrochemical technology

MFC - Microbial fuel cells

MSC - Microbial solar cell

NADH- Nicotinamide adenine dinucleotide reduced form

OEP- Oxygen evolution potential

OER- Oxygen evolution reaction

PEM - Proton exchange membrane

PMFC - Plant microbial fuel cell

rGO - Reduced graphene oxide

SC- Short circuit

SHE - Standard hydrogen electrode

SPEEK - Self-fabricated sulfonated polyether ether ketone membrane

TDS-Total dissolved solids

TSS-Total suspended solids

TOC-Total organic carbon

1. Introduction

Environmental contamination is continually increasing as the world's population continues to grow, which is accompanied by industrial and economic expansion [1,2]. Increasing demand for sustainable fuel, chemical production, and effective recycling of nutrients and metals is being driven by the unavoidable depletion of natural resources and ecological concerns [3]. It has become fashionable to look for fuel deficiency solutions in recent years. Carbon dioxide emissions are caused mainly by energy consumption, with worldwide CO_2 emissions from the combustion of fossil fuels reaching 33.1 gigatons in 2018. Therefore, finding a viable replacement for fossil fuels will be critical in lowering global CO_2 emissions [4,5]. This paved the path for developing environmentally benign, economically feasible, and long-term technologies to compensate for the energy problem through a more environmentally conscious approach. Because of this, researchers have been looking at renewable sources for the development of renewable fuels, energy, and chemicals in recent years [6,7]. Communicating microbes would be the most effective remedy to the current existent situation, which is critical owing to unabated human use and irresponsibility. They would also be the most effective response to future undiscovered man-made tragedies [8].

Bioelectrochemical cells (BEC) use microbial electrochemical technology (MET) to convert carbon-rich waste to bioenergy, nutrients, metals, or value-added chemicals [9]. An ion-exchange membrane (IEM) separates the BEC into two compartments: anodic and cathodic compartments. On the anode, electroactive microorganisms oxidize electron donors and reduce electron acceptors. Electrons are transferred from microbial cells to electrodes via extracellular medium components or electron shuttles melted in bulk solution. To maintain electroneutrality, ions pass across an IEM [10]. MET is used in microbial fuel cells (MFC) [11], microbial electrolysis cells (MEC) [12,13], and microbial electrosynthesis cells (MESC) [14]. The MFC is a quickly evolving expertise that can treat wastewater and retrieve energy in the form of

bioelectricity. MFCs can decompose a wide range of organic substances, allowing for treatment and resource recovery [15]. With external energy, bacteria may electrochemically convert inorganic carbon to biofuels and value-added chemicals such as biohydrogen, biomethane, acetic acid, and alcohols [13,16].

In the meantime, electroseparation and electroconversion processes have been proposed in wastewater treatment [17,18]. Electrosorption, capacitive deionization (CDI) and electrocoagulation could improve the separation of both inorganic and organic compounds compared to the physical (adsorption) or chemical (coagulation-flocculation) equivalent techniques [19–22]. Additionally, electroconversion technologies, such as electro-Fenton, anodic oxidation and the related systems, highlighted very high removal rates and yields of the organic pollutants, even the most recalcitrant ones [23–26]. Their coupling with BES/BEC could make them even more cost efficient and more sustainable.

In recent years, a number of review papers have helped solidify the study's main focus areas, including electron transport, electrode design, low-cost redox catalysts, role and microbial composition of biofilms, and practical applications. No systematic review comparing and assessing diverse BEC as green energy sources to harvest energy from waste/wastewater has been published. Electrochemical processes are found to be cost effective for water and wastewater treatment. The energy generated from BEC can be utilized as the energy source for the operation of electrochemical treatment. This review further discusses various BEC coupled energy systems, various critical factors affecting BEC performance, and challenges in scaling-up of coupled systems for long-term performance.

2. Bioelectrochemical cells

BEC combines electrochemically active microbes or other bio-catalysts with electrochemistry to promote reducing or oxidizing metabolic activity. BEC can generate electrical power or attain a reduction reaction by shifting electrons among an electron acceptor and an electron donor (Fig. 1). Michael Potter [27] initially researched the formation of bioelectricity by many microbes, which transform energy stored in the chemical bonds of the substrate into electrical energy via the breakdown of diverse substrates, mainly organic molecules from wastewater. BEC has gained popularity due to its eco-friendly and energy-saving properties [28,29]. Researchers have concentrated on improving electrode materials, designing BEC, and screening and isolation of electrochemically active bacteria (EAB) or inert model microbes to increase the applicability of BEC [29]. They are now widely used in pollutants removal, solid waste such as food waste degradation/processing, desalination, and materials research [7,30].

The voltage differential between the anode and the cathode acts as a driving force, causing current to flow between the two electrodes. The maximal voltage produced may be predicted theoretically based on biochemical reaction occurring in BEC, as given below:

Anode Reaction:

If acetate present in the wastewater,

$$CH_3COO^- + H^+ + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^-; E^{0'} = -0.296 \text{ V} \quad - \qquad (1)$$

Cathode Reaction:

If oxygen as electron acceptors,

$$O_2 + 8e^- + 8H^+ \rightarrow 4H_2O \quad ; E^{0'} = 0.816 \text{ V} \quad - \qquad (2)$$

If ferricyanide as electron acceptors

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \quad ; E^{0'} = 0.361V \quad - \quad (3)$$

Using the Nernst equation, the Gibbs free energy value corresponds to a theoretical cell voltage of

$$E_{cell} = \frac{-\Delta G_{cell}}{nF} = \frac{-\left(-842000\frac{J}{mol}\right)}{8mole^- x964 \ \frac{c}{mole^-}}$$

$$E_{cell} = E_{ca} - E_{an} \quad - \quad (4)$$

$$E_{cell} = 1.10V \quad - \quad (5)$$

where, ΔG is Gibbs free energy (−842000 J mol^{-1}), n is the no. of electrons released (8 e^-) and F is the faradays constant (96486 C mol^{-1}).

The MFC generates an utmost open-circuit voltage of 1.10 V as determined by the nicotinamide adenine dinucleotide reduced form (NADH) and pure oxygen reduction potential [31,32]. Nevertheless, it undergoes numerous losses such as activation, ohmic, and concentration losses and can achieve ~ 0.8 V in open circuit conditions and ~ 0.62 V during current generation [33].

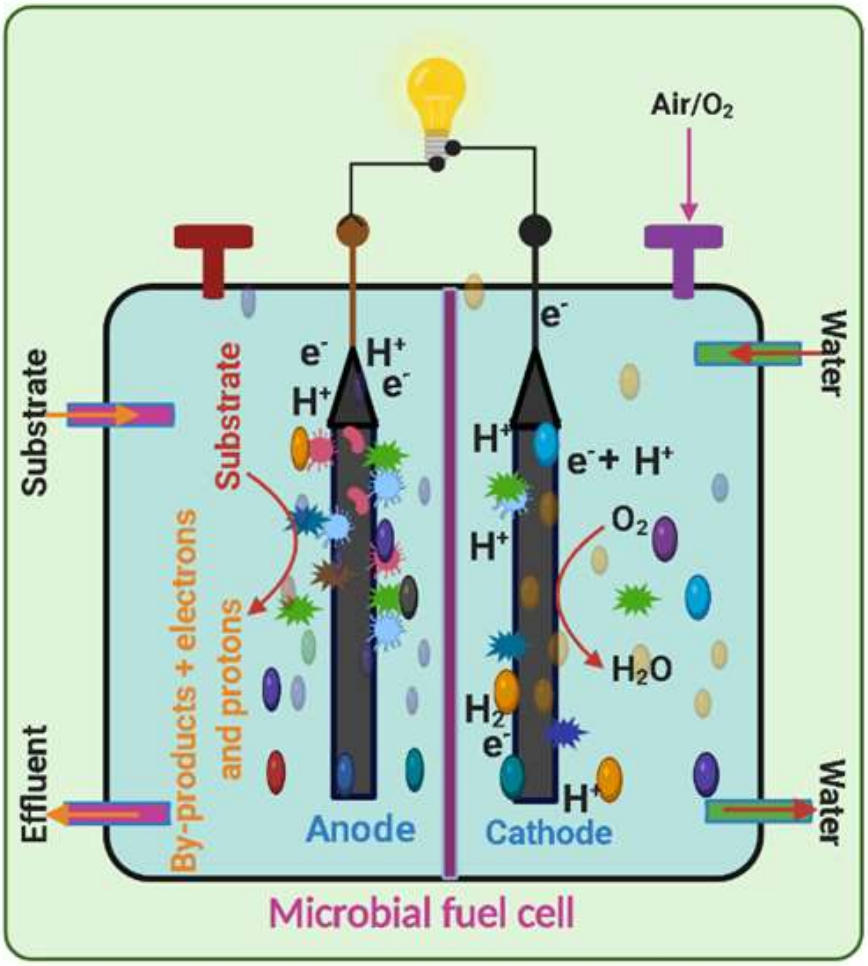

Fig. 1. Schematic illustration of double chamber microbial fuel cell (MFC).

3. Components of BEC

The most challenging issues in the construction of the BEC are identifying the most appropriate anode and cathode electrodes, membranes, and system designs that improve power production, coulombic efficiency, and treatment efficiency while minimizing cost and complexity [34]. For anode and cathode applications, electrodes must have excellent conductivity, good biocompatibility, low resistivity, chemically stable, and have adequate mechanical strength for the application [35,36]. Due to a different reaction taking place on the anode and cathode side, the electrodes should have some special characteristics as shown below:

- Anode should have a larger surface area which favors the bacterial attachment needed for the enhancement of power production
- The modified electrode surface area with a catalyst coating increases the oxygen reduction reaction rate in the cathode.

The BEC uses anodes made of different materials, including platinum, gold, titanium, and palladium, among others [37]. The use of noble metal-based materials as electrodes in MFCs may aid in the reduction of internal resistance. Because of the expensive cost of noble metals and their poor adhesions, carbonaceous electrodes such as graphite, carbon cloth and mesh, graphite rod, granules, and brush have been employed as electrodes in BEC for some time now [38]. Currently, nanocomposites-based materials (e.g. rGO, CNTs incorporated with other materials like polymers and metals) are used in the MFC due to its excellent conductivity, corrosion resistance, mechanical strength and thermal stability, etc. [39]. The material utilize in the anode can also be directly utilized on the cathode side of the MFC without any modifications. The common cathode materials are carbon paper, carbon cloth, carbon nanotubes, carbon brush, nickel, stainless steel, graphite plates etc. [40]. Several catalysts have been utilized to change the cathode electrode surface in order to boost power production. For example, platinum is the most often utilized catalyst because it lowers the activation energy of the cathodic reaction while increasing the reaction rate at the same time. But platinum is too expensive for being suitable for practical applications. Catalytic enhancement of the kinetics of oxygen reduction at the cathode has also been achieved using non-precious metals as catalysts [41]. As a result, the key difference in employing non-noble metals is the cost factor for future prospective large-scale BEC applications.

Both the anode and cathode compartments were separated by a membrane in the double chamber MFCs [42]. To transfer protons from the anode chamber to the cathode chamber in a BEC, cation exchange membranes (CEMs), also known as proton exchange membranes

(PEMs), are usually utilized. Nafion 117 is the most often used CEM. It is composed of a hydrophobic fluorocarbon backbone ($–CF_2–CF_2–$) with hydrophilic sulfonate groups (SO_3^-) attached, and 117 represents the membrane thickness of Nafion (a sulfonated tetrafluoroethylene copolymer) (0.019 cm). There are negatively charged sulfurate groups in Nafion that result in excellent conductivity for many different kinds of cations. Anode and cathode chamber pH splitting due to proton buildup, oxygen diffusion, substrate loss, and biofouling are the major issues with Nafion membranes; the solution to these issues is the use of a different membrane [43]. Anion-exchange membranes (AEMs) function better than CEMs because protons in the anode chamber are utilized by OH^- transmitted from the cathode without additional pH lowering. As a result, AEM has worse MFC performance because it encourages substrate crossover and biofouling development on the cathode surface. Many low-cost separators have been designed to improve BEC efficiency. These include a bipolar and a microfiltration membrane, porous fabrics, glass fibers, J-cloth, and an ultrafiltration membrane [44].

4. Classification of BECs

An electrochemical system is a collection of electrochemical replicas or devices that use various catalysts. BEC refers to a set of technologies utilized in biotechnology, such as producing power and valuable products. They fall into two types based on the catalyst used. The first uses microorganisms as catalysts, whereas the second uses enzymes.

4.1.1. Microbial electrochemical systems (MES)

Microbial electrochemical reactors can be classified into three major types: MFCs, MEC, and MESC. In recent years, researchers have also investigated a few other forms of BEC such as microbial solar cells (MSCs) [45], plant microbial fuel cells (PMFCs) [46], and microbial desalination cells (MDCs) [47]. Anode-cathode electron transfer in MFCs occurs as a result

of substrate oxidation in the anode chamber [48]. Due to their rapid degradation rate, many MFCs are capable of generating bioelectricity by utilizing numerous carbon-rich wastewater as potential substrates in the direction of pollution removal and energy generation [14]. Hence, the BEC design with a significant objective of wastewater treatment is widely known as bioelectrochemical treatment (BET) systems. Diverse bacteria, including *Shewanella putrefaciens*, *Shewanella oneidensis* MR-1, and *Escherichia coli* DH5α, have been effectively used in MFCs to generate maximum power densities ranging from 3800 to 4400 (mW m^{-2}) [14,49]. Furthermore, specific electrodes made of expensive materials such as gold, platinum, and other precious metals, increasing costs [14].

When compared to MFCs, MECs are essentially the inverse of that process. As previously stated, in MFCs, the substrate gets oxidized in the anode compartment. This oxidation process involves the release of electrons, which are simultaneously transmitted to the cathode compartment by a process that requires substrate reduction [50]. MECs rely on the potential positioned on the cathode compartment as the utmost critical aspect, and this is decided by the EAB and electron shuttles that have been supplemented, as they might have a variety of potential variances between them. Low energy efficiency and productivity with a slow rate [51] are also factors which hinder the expansion of MECs.

4.1.2. Enzymatic electrochemical systems (EES)

The enzyme electrodes act as external electron donors or acceptors. The EES is commonly employed in studies of electron transfer processes *in-vitro* because it only has one reaction, the enzymatic reaction, and the electron transfer kinetic potential is predefined [52]. Since electrochemical methods have been used to examine biological electron and ion transport with utmost attention and accuracy, it would be an economical and easy approach to study enzyme reaction kinetics [14]. *In-vivo* electron and proton transfer occurred when NADH: quinone

complex I was immobilized on the electrode as the sole electron acceptor [53]. Furthermore, the total output and electron transmission processes are still in the early stages of development.

5. Energy production mechanism

There are two methods in which bacteria can obtain energy in BEC. To begin, the primary pathway via which energy is generated is through the native respiration chain. In the environment, insoluble metals serve as electron acceptors for EAB [54]. The EAB like *Geobacter* and *Shewanella* are able to continually obtain energy by decomposing organic compounds for their cell growth and metabolic functions when introduced in BEC [14]. By dissolving insoluble metals in the anode, electrons are released to ensure the redox equilibrium [54].

In the second method, electrons are transferred. The discharge of a proton from a cathode into an intracellular compartment, together with the movement of electrons, is a possible method for the formation of ATP via the release of the proton motive force [14,55].

The MES process has been described differently based on its many capabilities, leading some researchers to refer to them as MXCs, where X stands for diverse uses [56]. The microbial activity and community dynamics in MESs are optimal when they are dynamic and efficient. They also have a greater substrate degradation rate, electron transmission efficacy, and reduced material and system charges. For this purpose, EAB are used in MESs [16,57]. Throughout their anaerobic respiration, these organisms convert the chemical energy of substrates to electrical energy, which is then used to produce electricity [58].

MESs can potentially convert any organic material into co-products by utilizing microbes as potential biocatalysts. Aside from the simple sugars and derivative products employed in maximum small-scale research, numerous complicated effluents have also been used, including

various wastewater from industrial and agricultural sectors, among others. One of the most important features of BECs for effluent treatment is the utilization of electrodes as non-exhaustible electron acceptors or even donors for pollutant breakdown [57]. Physical, chemical, or bioremediation processes require enormous amounts of energy or require external chemical additions. BECs can save money by lowering energy and chemical expenditures, which is important because normal cleanup techniques can take decades. Ideal anodic reactions in MESs usually have a lot of effectual microbial metabolism and community, a high rate of substrate reformation and electron transport efficacy, and less material requirement.

6. Factors affecting energy production

6.1. Electrode material

Anode material has been extensively investigated, leading to many detailed review publications. Microbial anodes made of carbon-based materials are by far the most popular. Because of their low electrical conductivity, large surface areas would require metallic current collectors. Metallic anodes are so intriguing options. The ability of stainless steel to create foam microbial anodes has shown promising results, notably in the field of biotechnology [59]. However, excessive salt concentrations affect the possibility of pitting corrosion. The anode's potential must be precisely managed to prevent corrosion [60]. These ions are lethal to bacteria. Copper-polymer hybrid composites might be an option. Titanium is recognized to be undesirable for anode applications due to its poorly conducting passivation layer. To create dimensionally stable anodes, titanium coated with metal oxides like ruthenium and tantalum oxides are used [59]. Only a few research has developed dimensionally stable anodes supporting microbial anodes.

Several researchers in the field of BEC have also looked into the choice of material for the cathode of MECs. Platinum is very overpriced, and it loses a lot of its ability to generate H_2 at the neutral pH values that are required by biocathodes [61,62] . Alloys made of stainless steel, nickel, and cobalt have been found to be good candidates, even though they are still very expensive. Porous materials have been suggested as cathodes for MECs to generate more H_2 as the porous materials provide large surface area for enhance cathodic reaction. This solution may work on laboratory scale, but it can't be used for very high current density [63]. At high current density, bubbles cover the surface of the interstitial electrolyte, which reduces the effectual conductivity and then coalesces in the pores, obstructing the electrode performance. Unless the electrolyte is circulated through the porous electrode via pumps/pressure, it is not a good idea to use it on an industrial scale [59]. Long-term functioning of cathodes can result in considerable degradation of their functionality due to salt precipitation, which when combined with biofouling, can result in typically 20 to 40 percent reduction in power density throughout the course of the operation [64]. However, even if the biofilm layer on the cathode may be cleaned by merely rubbing it off, the construction of a large-scale unit comprised of multiple stacked modules must allow for the quick and easy dismantling of separate components to allow for easy cleanup [65].

6.2. Microbial metabolism and cell potential

Mitochondrial respiration is characterized by the oxidation of organic matter (feed) by a number of electron donors, with O_2 serving as an electron acceptor in the anaerobic metabolic reaction. Inorganic substances are oxidized in the presence of dehydrogenases, which are found in plasma membranes. Within a MFC, prothetic groups help to facilitate the flow of electrons between electrons [66]. Photosynthetic bacteria (or algae), on the other hand, utilize high-energy photons such as those emitted by chlorophyll pigments and liberate electrons through the function of quinones and bacteriopheophytins [67].

There are oxidation and reduction reactions at both the anode and the cathode electrodes that make up the cell potential in MFCs. In MFCs, the use of different carbon-rich substrates for microbial growth affects its power output. Because of the O_2 reduction reaction, the catalyst on the surface of the cathode affects the power generation capacity of the MFCs [68]. Ohmic behavior, activation potential, concentration potential, bacterial metabolism, and pH, all have an effect on output power of MFCs [69]. A lot of different types of microorganisms are responsible for producing bioenergy in MFC technology according to earlier research. In MFC technology, mixed culture and bio-electrochemical selection procedures can be used to increase the amount of power produced.

6.3. Substrate

A variety of organic substrates used for EAB growth affect the effectiveness of MFCs. For microbial metabolism, there are a variety of carbon-rich organic substrates that may be used including acetate, glucose, butyrate, starch (cellulose), phenol and arabitol etc. [70]. Increasing the output of MFCs by utilizing lignocellulosic biomass as a substrate is a common practice. Carbon-rich wastewater from starch processing is rich in carbohydrates, proteins, and starch, which makes it suitable for MFC technology [47]. Knowledge of how each aspect affects MFC performance is essential to a successful design. In addition, before deciding on a design, it is necessary to know the impact of several elements on the performance of an MFC. Because of this, effort to get a deeper understanding of the system and its numerous components is necessary to manage the efficiency and kind of energy generated [2].

Further, by utilizing carbon-rich wastewater as a possible substrate instead of the synthetic substrate like glucose in BEC will leads to drastic reduction in the overall cost of the entire MFC process for electrogenesis. Numerous investigators have evaluated the MFC performance with waste/wastewater as a potential carbon-rich substrate. Electrogenesis from numerous wastewater employing mixed culture and a single strain of *Shewanella oneidensis* in

the single-chamber MFC is found much more effective [71]. It is also reported that higher current production is independent of substrate degradability [72]. At increasing COD concentration, power production is also reduced, which may be because of substrate-mediated suppression of microbial growth. This is a common finding in the literature [73,74]. A major factor influencing substrate inhibition is bacterial kind and hydrolysis capabilities, both of which must be determined.

6.4. Salinity

The conductivity of ions and the production of electricity in BEC depend on the existence of salts [69]. High conductance has influence on the transport of protons across the cation exchange membrane make saline effluents ideal for BEC [10]. When sodium acetate and sodium chloride were added to an anodic chamber, the addition of sodium chloride increased power production while decreasing internal resistance. In addition, salt boosted power output by 30% while decreasing internal resistance by 33%. MFCs' performance was observed to improve when a redox mediator was added. A cathode treated with particular catalysts boosted electricity production and reduction activities. High salinities at the anode tend to hinder the functioning of an EAB when they exceed the optimal value [75]. Further, the metabolic activities of EAB were inhibited at anodic surfaces using fruit, vegetables, and dirt in a composite MFC, resulting in a drop in power density. Since EAB cannot handle high salinity, it should be kept under control to avoid stressing them, but not too low to do them harm [69].

6.5. Biofilm redox properties

Effective electrocatalytic layer formation has been a key focus of electrochemical engineering research and innovation [76]. BEC's catalytic layer, in contrast, forms naturally on electrode surfaces, and the researcher has only little control over how to direct this biofilm to

perform the desired function [77]. In a multispecies media, the goal is always to find how the biofilm can be manipulated to choose the most efficient EAB or to compel it to produce the most conductive matrix possible. These may be achieved with the aid of the applied potential, although it may not always be successful. That is still up for discussion. Ultra-microelectrodes can also boost the EAB biofilm matrix's electron transfer capability [76]. As a popular research area, understanding the underlying principles of electron transport in anodes is now being pursued; however, literatures on strategies for maximizing the biofilm's performance are still inadequate [68].

7. BEC coupled electrochemical systems

7.1. BEC combined with electrosorption

The electrosorption offers the advantage of being a low voltage electrochemical technology that allows enhancing adsorption on a porous conductive polarized material by promoting electromigration for ionic compounds and molecules displacement for uncharged molecules [78–80]. Applied current intensities are required to be in the capacitive domain to avoid parasitic reactions that occur with faradaic currents, such as water oxidation or reduction reactions [81]. In this condition, the electrode potential needs to be below 1.4 V/SHE and higher than 0.4 V/SHE [82]. This low-voltage technique allows utilizing activated carbon-based electrodes as both cathode and anode, which can be an advantage in enhancing anodic electrosorption [78]. Contrastingly, the carbon would be corroded when used as an anode in faradaic conditions. Electrosorption has been particularly used to remove organic pollutants (e.g. phenolic compounds) [83], inorganic salts (e.g., fluoride) [84] and metals/metalloids (e.g., arsenic) [85,86] from water and wastewater. The polarized adsorbent material can then be regenerated by electrodesorption, using polarity reversal technique.

Considering that the BEC system, for example, MFC produces a cell potential around 0.5 – 0.8 V, the combination between MFC and electrosorption arose particular attention in the last decade thanks to the possible synergies [82]. This self-powered combined technology could be a mild and green alternative to remove water contaminants. Metal such as copper could be removed from industrial wastewater by MFC-electrosorption combination (Fig. 2a) [87]. Electrodes made of activated carbon fibers (4 cm^2) have been implemented for electrosorption, whose gap was 3.5 cm. Cu^{2+} electrosorption increased with its initial concentration (5– 100 mg L^{-1}) and the number of MFC in series (1–3). A 1.8-times increase of efficiency was obtained between MFC-electrosorption and adsorption alone. However, faradaic reactions led to the formation of CuO and Cu through redox reactions with Cu^{2+}.

Organic pollutants were also removed by MFC-electrosorption combination [88–92]. 99% of oxytetracycline was eliminated using 3 MFCs in series combined with electrosorption using ACFs working electrode [89]. This 3D electrode was reused for several cycles of electrosorption, but the removal percentages decreased with the cycles number. A similar combination of MFC with electrosorption using ACFs electrodes could remove phenol (100 mg L^{-1}) with an increase of 42% compared to adsorption alone [91]. Implementing 3 MFCs in series could even improve the electrosorption capacity from 1.46 mmol g^{-1} to 1.76 mmol g^{-1} [90].

Considering that the electric double layer and mass transport have been identified as the two main phenomena that affect the electrosorption efficiency [78], enhancing these mechanisms could improve the process. Implementing thin-film microreactors could improve the transport of metals and organic contaminants in wastewater, and reduce the energy consumption [93–97]. Moreover, the reactive electro-mixing concept and reactors might be suitable for such hybrid systems to enhance both transport and electric double layer in micro-

electroblades, while increasing the treatment capacity thanks to the microreactor [98]. This remains to be tested.

MFC coupled to electrosorption of inorganic ions has been more used for water desalination context. In this condition, electrosorption has been renamed as capacitive deionization, while its coupling with MFC is discussed in the following section.

7.2. BEC combined with capacitive deionization (CDI)

Capacitive deionization has gained a huge boost in the last twenty years as a promising alternative to competitive commercial technologies that require high-pressure (e.g., reverse osmosis) or high-temperature (e.g., evaporative concentration) systems for water desalination [99,100]. The synergy obtained by combining MFC and CDI is attracting attention. Two reactor configurations can be considered, either two sequential reactors or a hybrid system in which both MFC and CDI can occur, namely a capacitive microbial desalination system [82].

Different connection types of MFCs have been tested in combination with CDI, i.e. single, series and parallel configurations [101]. The latter option showed higher voltage generation (0.63 V), while the conductivity removal was around 60% for low salt concentration (50–150 mg L^{-1}) wastewater. A detailed study about circuit arrangement highlighted the importance of considering the electrical characteristics and the operating conditions (Fig. 2b) [102]. The parallel configuration was found optimal with MFCs having higher internal resistance (146 Ω), while the series connection surpassed using lower resistance (12 Ω) MFCs. The desorption mode has been also varied, either the discharging mode or the short circuit (SC) mode were tested [103]. The DC mode offered better desalination rate (NaCl) (200 mg $(L\ h)^{-1}$) than SC mode (135 mg $(L\ h)^{-1}$). However, the current was higher in DC than in SC mode. Still, the energy stored in CDI cell as electrostatic energy could be reused for MFC thanks to the DC mode.

Other variants of MFC/CDI have been proposed. The ion exchange membrane configuration demonstrated strong influence on MFC-CDI performance [104]. In addition, a supercapacitive desalination cell that consists of implementing MFC as either cathode or anode of an internal supercapacitor could improve the MFC/CDI performance [105]. This allowed generating 3 W m^{-2} of power, while the conductivity decreased by 60% without pH change.

The matrix effect should be studied more in detail as it can strongly influence the electrochemical process efficiency [82,106–108]. For example, the presence of organic compounds could compete with inorganic salts for adsorption sites in CDI. Moreover, scaling and biofouling are major drawbacks that need to be addressed. Finally, the scale-up of such hybrid systems remains the biggest challenge, while keeping constant the power density output and the high removal efficiency whatever the entrance flow composition and rate. Considering the low versatility of biological-based systems like MFCs towards the water and wastewater composition (pH, organic content, etc.) [109], this latter point is a crucial issue.

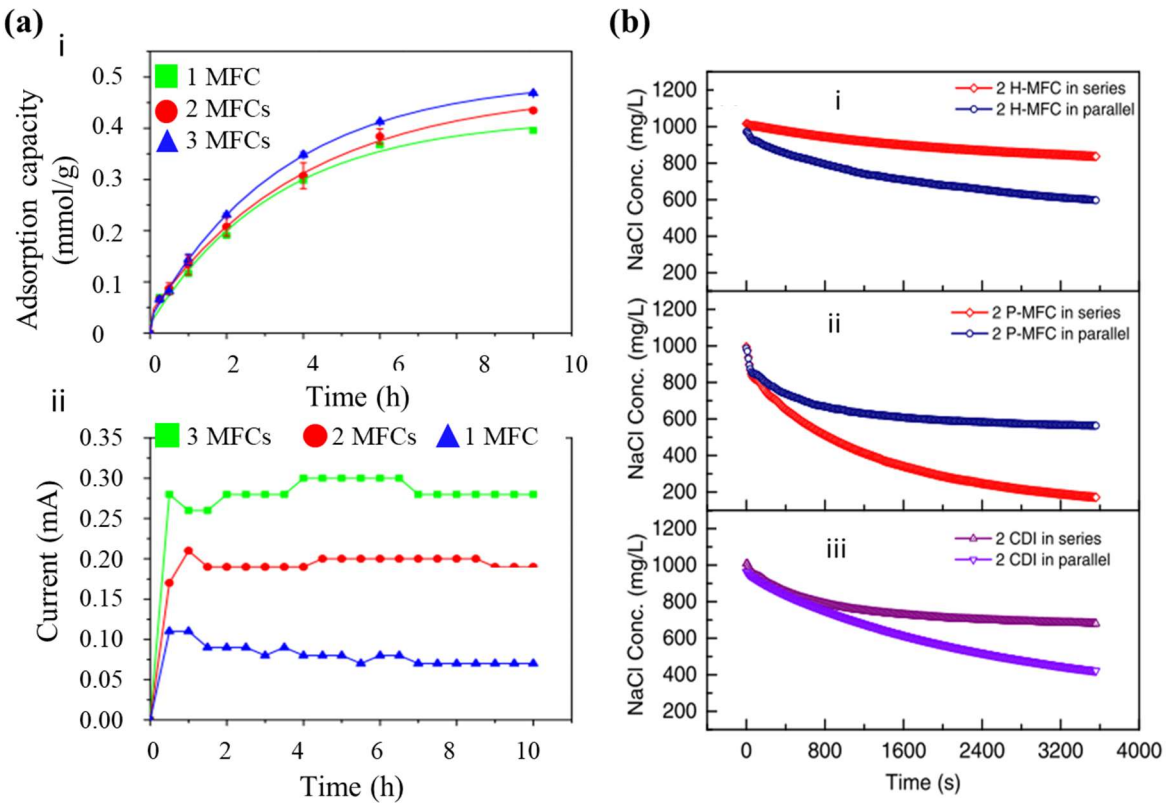

Fig. 2. (a) Influence of MFCs arrangement on the adsorption capacity (A) and current (B) (Reprinted with permission from [87]. Copyright 2016, Springer), (b) desalination curve with different MFC-CDI cells configurations (series or parallel) and internal resistances (Reprinted with permission from [102]. Copyright 2015, Elsevier).

7.3. BEC combined with electrocoagulation

Electrocoagulation (EC) process has gained much consideration owing to its ability to remove all water pollutants [110–112], to treat municipal wastewater [113], landfill leachate [114], industrial wastewater [115–120] including mixed industrial wastewater [121,122] with lesser cost. MFC is found as an effective source of energy for the operation of the EC process [123,124]. However, only a few studies are reported this theme. Mei et al. [124] used this system (Fig. 3a) for the treatment of bilge water and found 93% of oily organic removal, which has similar efficiency to EC system operated on DC power supply. Electrocoagulation and electro floatation processes contributed to the effective removal of oily organic matter from the

bilge water, as reported earlier [125]. The open-air cathode in MFC was made of 30 percent water-proof carbon cloth with four polytetrafluoroethylene diffusion layers and one catalyst layer (0.5 mg Pt cm^2), with the anode being made of graphite fibre brush. EC process electrodes were made of aluminum plates, which were connected together with electrical wires. Either acetate or municipal wastewater was employed as a potential substrate in MFC and more than 80% of COD removal was observed along with sufficient power generation for the operation of the EC process.

Similar to this, an interesting study on wastewater treatment by MFC-EC is reported by Safwat [123]. Mei and co-workers [124] used three MFC units to generate the power required for the operation of EC. At the same time, Safwat [123] used batteries to store electricity generated from MFC and used for the operation of EC. Graphite fiber felt was used as electrodes in MFC and the electrode from the working MFC was used as the anode to facilitate the start-up. In the EC process, aluminum plates and stainless steel were utilized as anodes and cathodes, respectively. Initially, the experiments were conducted in synthetic wastewater with an initial COD of 1000 mg L^{-1}. It was found that the MFC can reduce its 43.4% of COD with 72 h of operation along with peak power generation of 3.3 V at 60 h of operation. Even though the voltage declined after 60 h of operation, the voltage was above 2.4 V after 36 h. Thus, two batteries of 1.2 V were used for storing the power generated. However, power generation from municipal wastewater is lesser than that of synthetic wastewater. The peak voltage was 1.86 V and hence a 1.2 V battery was used for storing the power generated. Even though the power generated from municipal wastewater is less, the efficiency of the combined system is comparable in both cases. COD, TDS, and TSS removals from synthetic wastewater were observed as 95.4%, 88.4%, and 93.8%, respectively and it was 83.7%, 57.5%, and 85.8%, respectively for municipal wastewater.

Interestingly, Dong and co-workers [126] reported the application of a biocathode-EC system (Fig. 3b) with iron anode, which can remove algae from the water, and carbon-graphite fiber brush biocathode which can remove NH_4^+-N from water. The system can generate electricity in addition to pollutant removal from an aqueous medium. NaCl addition as an electrolyte is found to have a significant impact on the performance of the biocathode-EC system. Maximum power density enhancement from 8.41 W m^{-3} to 11.33 W m^{-3} and open-circuit voltage increase from 0.478 V to 0.495 V with 1 g L^{-1} NaCl addition was observed. In the biocathode chamber, more than 50% NH_4^+-N removal with a higher than 6.7 mg L^{-1} h^{-1} nitrogen removal rate was observed and the presence of nitrifiers such as *Nitrosomonas*, *Nitrospira*, *Nitrosococcus*, and *Nitrobacter* revealed the microbial-catalyzed nitrification process in the biocathode chamber. Almost complete removal of algae was attained in EC chamber and is mainly due to (1) electrocoagulation, (2) sedimentation of algae (negatively charged) due to loss in electrostatic stability with the electrolytic generation ferrous ions from anode (as in the case of double-layer compression mechanism in coagulation process), (3) oxidation of coenzyme A (CoA) and (4) electro-oxidation of algae adsorbed over the anode surface.

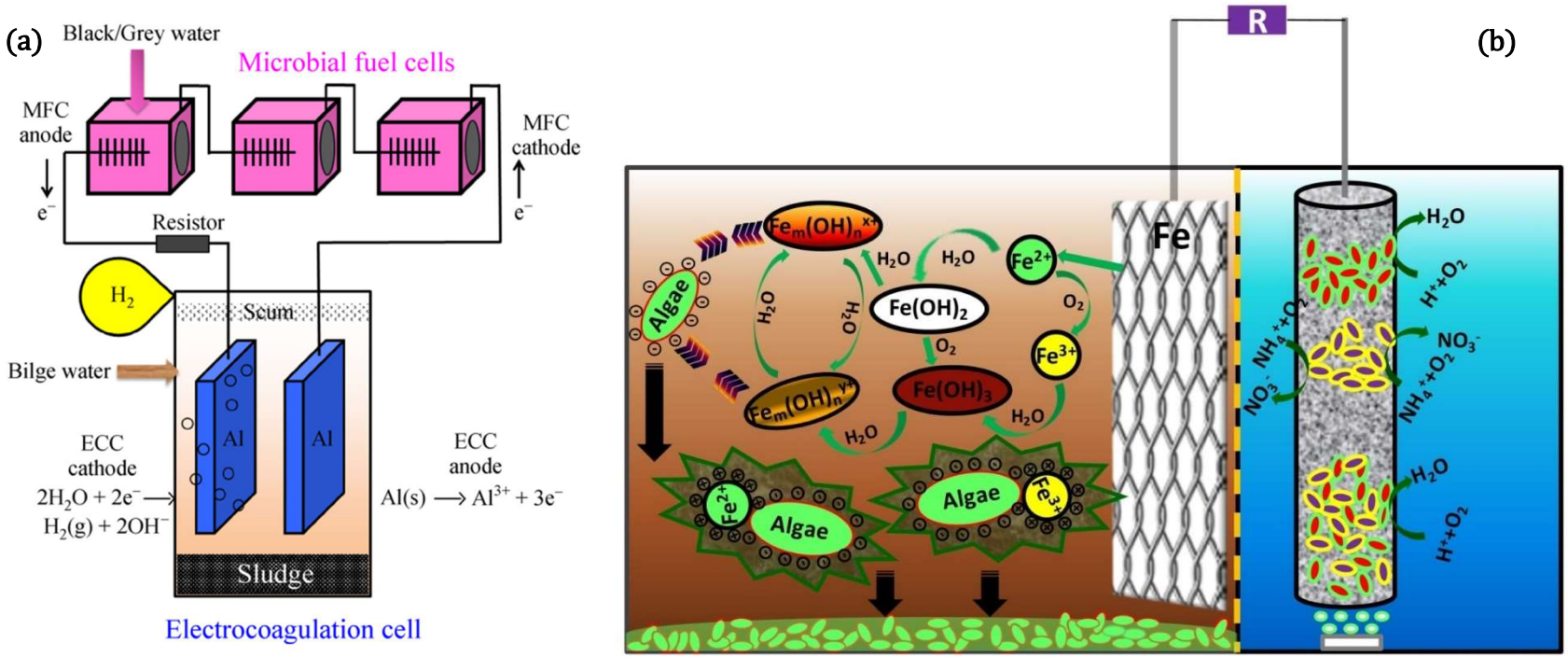

Fig. 3. (a) MFC-EC system, Reprinted with permission from Ref. [124], Copyright © 2019, Higher Education Press and Springer-Verlag GmbH Germany, part of Springer Nature (b) biocathode-EC system, Reprinted with permission from Ref. [126] Copyright © 2017 Published by Elsevier B.V.

7.4. BEC combined with electro-Fenton (EF) related processes

BEC coupled EF is a smart zero energy wastewater treatment where the biomass energy stored in wastewater as organics are converted to electricity by the microbial activity at the anode in the BEC and the electricity generated simultaneously driven an *in-situ* or *ex-situ* EF reactor [127–129]. This is an effective, efficient and economically beneficial way for remediation of pollutants from wastewater and contaminated soils since the system is self-powered and requires no external energy supply. The EF wastewater treatment is coupled with BEC either *in-situ* where the electricity generated by BEC powered EF reactions in the cathodic chamber/region of the BEC or *ex-situ* in which the electricity of BEC is connected directly to external EF reactor (Fig. 4) [130–132]. Note that in BEC – *in-situ* EF, the hydrogen peroxide required for Fenton's reaction is generated by two electrons reduction of dissolved oxygen at the cathode chamber of the BEC, with electrons supplied by the microbial oxidation of the organics at the anode surface [133]. The activation of H_2O_2 is achieved either by adding catalytic quantity of Fe^{2+}/Fe^{3+} (homogeneous catalysis) or solid Fe sources (iron oxides, sulfide and others) as Fenton catalyst into the cathode chamber prior to electrolysis [132,134,135]. The iron source can be loaded on the cathode of the BEC to form heterogeneous EF, which make the EF more effective over a wide pH range and enhance the reusability of the catalyst [131,136,137]. Note that when the solid iron source or iron-loaded cathode is used in the EF chamber of BEC-EF, both homogeneous and heterogeneous catalytic decomposition of H_2O_2 to reactive oxygen species occurs depending on the pH of the cathode chamber and the properties of the solid iron source [132,138,139]. The predominant mechanisms during the EF using solid iron sources depend on the amount of leached Fe^{2+}/Fe^{3+}ions which is responsible for the homogeneous EF process [138,140,141].

BEC – *in-situ* EF systems are the most investigated configuration of BEC-EF because of its compactness and ease of operation. Besides, powering external EF reactors by electricity

generated by BEC is very limited in literature because of the low output energy of the system, which limit the capacity of the EF reactor (electrode size and treated volume) [130,131]. Indeed, studies that have reported BEC-*ex-situ* EF have mainly powered mini-EF reactors (<100 mL) with low electricity supply to the reactor [142,143].

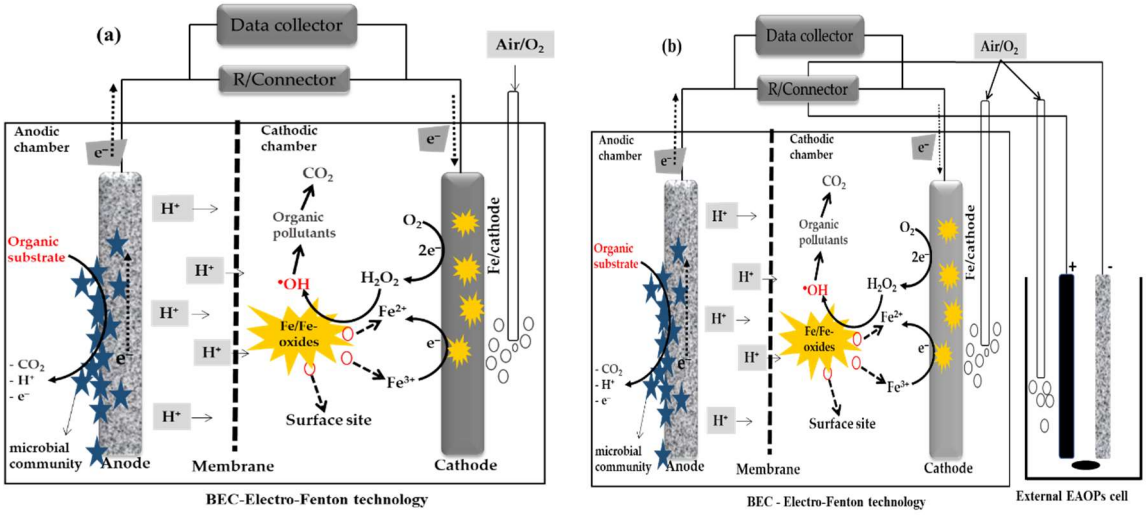

Fig. 4. Scheme of mechanisms of operation (a) BEC-*in-situ* EF and (b) BEC-*ex-situ* EF (Adapted from ref. [132] with modification).

BEC-EF is a well-studied wastewater treatment technique for the remediation of organic and inorganic pollutants from a wide range of different classes of industrial wastewater, synthetic wastewater and contaminated soils and some review articles that summarize some of these studies are available in the literatures [127–129,139]. Both homogeneous and heterogeneous EF have been coupled with BEC for wastewater and contaminated soils remediation. For example, dual-chamber BEC-EF using $FeSO_4.7H_2O$ as iron source was utilized for the degradation of paracetamol in the cathode chamber with simultaneous generation of electricity by the microbial oxidation of domestic wastewater at the anode chamber [144]. The BEC-EF achieved 70% and 25% degradation and mineralization of 10 mg L^{-1} paracetamol solution, respectively, after 9 h of treatment with an average current density generation of 757.41 ± 65.47 mA cm^{-2}. Antibiotic sulfamethoxazole solution was also treated

by continuous flow BEC-EF using CNT/γ-FeOOH modified stainless steel cathode and carbon cloth [145]. At initial 25 mg L^{-1} concentration, 94.66% sulfamethoxazole was degraded after 48 h of treatment with simultaneous generation of up to 283.32 ± 16.35 mA cm^{-2}. Hassan et al. investigated BEC-EF using M-type strontium hexaferrite nanoparticles as energy-efficient technique for the degradation of three antibiotics (Sulfaquinoxaline (SQX), Tylosin (TYI) and Tetracycline (TC)) [146]. The couple technique degraded 10 mg L^{-1} of these antibiotics in 17 h, and whole degradation was attained within 24 h with total organic carbon removal of 74.8–87.2% and maximum power output of 136.4 ± 3.1 mW m^{-2}. Comparative homogeneous BEC-EF using Fe_2SO_4 as Fenton catalyst showed lower catalytic efficiency, achieving 20% lower degradation of antibiotics in 24 h. Emerging contaminants including Bisphenol A (BPA), Estrone (E1), Sulfamethazine (SM2) and Triclocarban (TCC) degradation was investigated using BEC-EF equipped with graphite rod/stacked graphite granules cathode and Fe^{2+} as Fenton catalyst [147]. The BEC-EF system exhibited degradation efficiency of 100%, 75%, 98% and 97% for E1, BPA, TCC and SM2, respectively, after 24 h in a continuous flow reactor. BEC-EF systems have also been studied as an effective technology for the degradation of other pharmaceuticals such as Tetracycline Hydrochloride [148], Triphenyltin Chloride [149], 17β-Estradiol and 17α-Ethynyl-Estradiol [150] and Norfloxacin [151]. In all cases, the H_2O_2 electrogenerated was catalytically activated to $^{\bullet}OH$ by leached Fe^{3+}/Fe^{2+} and solid Fe^{III}/Fe^{II} redox couples at the surface of the cathode. The use of heterogeneous $Fe@Fe_2O_3$ or $FeOOH/TiO_2$ modified cathode allows the BEC-EF to operate over a wide pH window.

Synthetic dye solutions remediation has been extensively studied by the BEC-EF systems using either homogeneous or heterogeneous Fenton catalysts. For example, Zhuang et al. [152] investigated BEC-EF using $Fe@Fe_2O_3$/carbon-felt composite cathode for simultaneous oxidation of wastewater at the anode and cathodic degradation of Rhodamine Blue (RhB) by Fenton's reaction. The BEC-EF system was able to achieve 95% and 90% RhB solution

degradation and TOC removal efficiency, respectively, after 12 h of treatment with simultaneous production of 65.2 μA cm^{-2}. Cathodic degradation of Acid Orange II using $FeVO_4$ in Fenton-like reaction was studied in BEC-EF system with a maximum power generation of 15.9 W m^3 at the initial solution of pH 3 and 0.8 g $FeVO_4$ in the cathode chamber [153]. The cathodic Fenton's oxidation achieved 89% and 81% dye and COD removal efficiency, respectively. Both the Fe^{III}/Fe^{II} and V^{V}/V^{IV} redox couples activated the electrogenerated H_2O_2 to $^{\bullet}OH$ in Fenton and Fenton-like reactions as described in Eq. (1–4).

$$Fe^{(II)} + H_2O_2 \rightarrow Fe^{(III)} + {}^{\bullet}OH + OH^- \quad (1)$$

$$Fe^{(III)} + H_2O_2 \rightarrow Fe^{(II)} + {}^{\bullet}OOH + H^+ \quad (2)$$

$$V^{(IV)} + H_2O_2 \rightarrow V^{(V)} + {}^{\bullet}OH + OH^- \quad (3)$$

$$V^{(V)} + H_2O_2 \rightarrow V^{(IV)} + {}^{\bullet}OOH + H^+ \quad (2)$$

The BEC-EF using $Fe@Fe_2O_3$/activated carbon felt composite cathode was also reported for the degradation of RhB solution at pH 3 with concurrent production of maximum power density, current density and voltage of 16.7 W m^{-3}, 36 A m^{-3} and 900 mV, respectively [154]. After 24 h, the cathodic RhB degradation efficiency was 95.0 ± 3.5% at RhB concentration of 10 mg L^{-1}, external resistance of 120 Ω, air flow rate of 0.3 L min^{-1} and cathodic pH of 3. Azo dye Orange G [155] and *p*-Nitrophenol [156] degradation using BEC-EF was studied using Fe^{2+} ($FeSO_4$) and limonite as an iron source, respectively. Limonite as heterogeneous catalyst was stable over 7 cycles of usage at 112 mg per 50 mL, achieving > 94% degradation efficiency for p-Nitrophenol in 6 h. In contrast, BEC-EF using Fe^{2+} was not reusable as a homogeneous catalyst but achieved complete degradation and up to 87% mineralization of 400 mg L^{-1} Orange G solution in 6 h. BEC-EF using Fe^{2+} was also utilized for the cathodic degradation of 75 mg L^{-1} Amaranth solution [157]. Amaranth degradation efficiency of 82. 59% was achieved after 1 h at 1 mM Fe^{2+} along with maximum power output of 28.3 W m^{-3}. Other studies have

demonstrated the superior efficiency of BEC-EF for the degradation and mineralization of Methylene Blue [158], Acid Orange 7 [159], Methyl Orange [160] and phenolic compounds – Syringic Acid (SA), Vanillic Acid (VA) and 4-Hydroxybenzoic Acid (HBA) [161]. Complete degradation of all these pollutants by cathodic EF were reported in all cases with enhanced power generation.

Although real wastewater of different classes is anodically degraded by microorganisms' activity in BEC for electricity generation, some studies have investigated cathodic degradation of real wastewater by Fenton's reaction in BEC-EF systems. The use of real wastewater as a target pollutant to investigate the efficiency of technology is essential because it depicts the exact situation encountered in real field applications compared to simulated wastewater. For example, Birjandi et al. [162] reported enhanced medicinal herbs wastewater treatment in continuous flow BEC-EF using Fe@Fe_2O_3/graphite composite. A maximum COD removal efficiency of 93% and BOD_5/COD of 0.89 was achieved after 83.33 h with maximum current density, voltage and power density production of 603.86 mA cm^{-2}, 892 mV and 183.06 mA cm^{-3}, respectively. BEC-EF using five stacked Fe@Fe_2O_3/carbon felt composite plates cathode has also been studied for the treatment of swine wastewater [154]. Without any external energy supply to the system, BOD_5, COD, NH_3-N and TOC in the wastewater could be significantly reduced at both 1.1 g COD L^{-1} d^{-1} and 4.6 g COD L^{-1} d^{-1} of organic load rate, with the overall removal rates ranging from 62% to 95.7% and simultaneous maximum output power density generation of 3–8 W m^{-3}. BEC-EF was also utilized for the treatment of dairy and oily wastewater simultaneously using $FeSO_4$ as the iron source and carbon felt cathode [163]. Effective degradation of organics was achieved by the BEC-EF system under Fenton's condition using anion exchange membrane due to pH stabilization, attaining 77% COD removal efficiency and 260 mW m^{-3} after 183 h of treatment. Other studies have utilize BEC-EF for cathodic degradation of glucose [164], coal gasification wastewater using $FeVO_4$

modified carbon felt [165] and diary wastewater using N-doped carbon/Fe_3O_4 cathode [166]. The BEC-EF achieved 34.15% degradation of glucose, 83.7% and 78% COD removal efficiency for coal gasification and diary wastewater, respectively.

BEC-EF using γ-FeOOH as Fe^{2+} source was utilized for the removal of arsenite (As(III)) from wastewater [167]. The decay of the As(III) during the BEC-EF treatment was strongly influence by the presence of γ-FeOOH and dissolved oxygen, with the As(III) solution significantly decreased with treatment time while As(V) concentration sluggishly accumulated during the 48 h treatment. Completely removal of 1 mg L^{-1} As(III) was achieved within 120 h of treatment at 0.208 h^{-1} and calculated current efficiency of 73.1%. Another application of BEC-EF recently reported is water disinfection/inactivation of pathogens including *Escherichia Coli*. Zhou et al. [168] utilized BEC-EF with graphite plate cathode and Fe^{2+} (iron source) as highly efficient technology for *Escherichia Coli* inactivation in synthetic wastewater. The *E. Coli* was destroyed and mainly inactivated by $^{\bullet}OH$ generated from Fenton's catalytic decomposition of H_2O_2 by Fe^{2+} in the cathode chamber (Fig. 5). BEC-EF system achieved 4-log reduction of *E. Coli* (10^7 to hundreds CFU mL^{-1}) with an external applied voltage of 0.2 V, 0.3 mM Fe^{2+} and cathodic pH of 3.

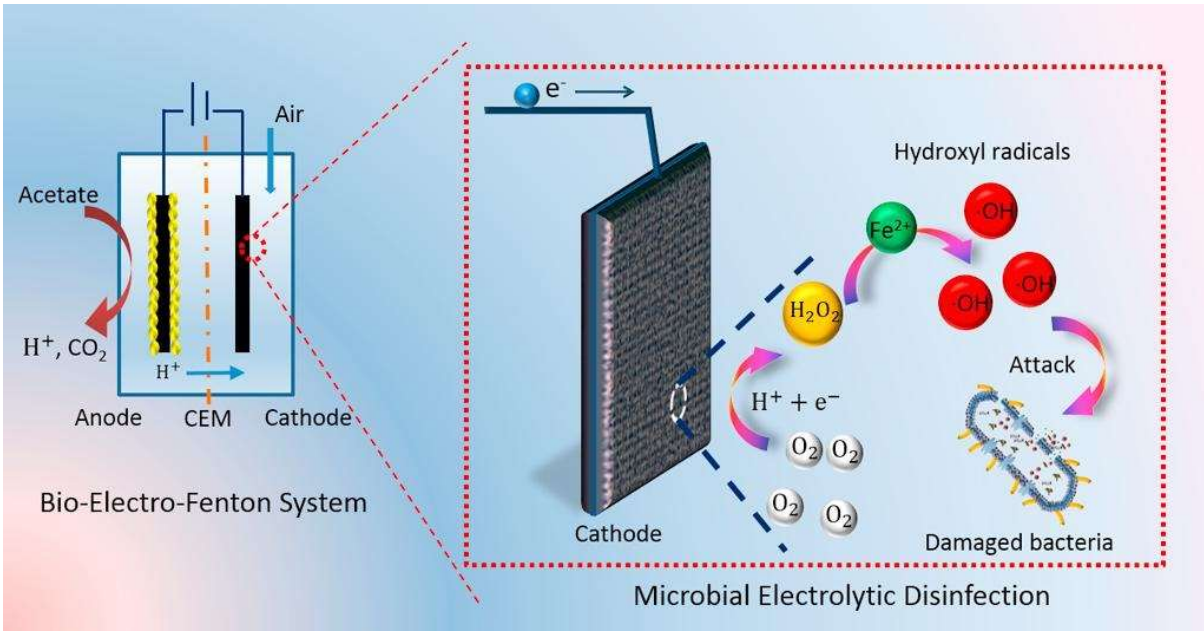

Fig. 5. Schematic of application of BEC-EF for water disinfection. (Reprinted with the permission of ref. [168], Copyright © 2018 Elsevier B.V.)

BEC – *ex-situ* EF technology is not as common as *in-situ* EF because of the low electricity output of BEC, which is not capable of powering average electrolytic reactors. Indeed, BEC power electrooxidation is limited in literature because it is an electrode process that requires higher electric charge for electrode activation and water oxidation to generate reactive species [131,132]. Nevertheless, mini-EF reactors were powered by electricity generated by benthonic BEC-EF system for the degradation of 50 mg L^{-1} Reactive Black 5 (RB5) using 150 mg L^{-1} iron and continuous air supply in the mini 4 mL reactor for the generation of H_2O_2 [143]. The dye decolorization in the external EF reactor was 90%, 85% and 82% after 160 h of electrolysis at 30, 50 and 70 mg L^{-1} RB5 concentration with 1035-1046 voltage supplied by BEC-EF. The same authors previously reported the powering of two *ex-situ* EF reactors (batch and continuous EF reactors) by the electricity generated by BEC-EF for the degradation of Lissamine Green B (*ex-situ* EF) and mixture of Lissamine Green B and Crystal Violet (*in-situ* EF in BEC cathode chamber) [169]. The BEC-EF (*in-situ*) system was able to generate stable electricity that was enhanced by the cathodic Fenton's reaction, reaching a stable voltage of

approximately 1000 mV. The *ex-situ* EF batch and continuous reactors powered by BEC-EF achieved up to 98.3% decolorization of Lissamine Green B, indicating the efficacy and potential of this technology for wastewater treatment. Zhu and Logan [142] utilized electricity generated by BEC system as a renewable power source for driving external anodic Fenton's reactor for the degradation of organic pollutants. The low voltage power source (600 mV) of the BEC simultaneously accomplished H_2O_2 generation and Fe^{2+} release from the iron anode for Fenton reaction. The anodic Fenton process powered by BEC was able to achieve complete phenol degradation studied as a targeted pollutant with 75 ± 2% TOC removal in one cycle of 22 h treatment. BEC-powered external anodic Fenton reactor was also investigated for the degradation of Acid Orange II using iron as a sacrificial electrode [170]. The generated electricity in the BEC system (444 mV) accelerates the H_2O_2 generation and Fe^{2+} release from the sacrificial electrode. After 30 min of treatment, 85% of the dye was degraded in the BEC-anodic Fenton reactor, which is far higher compared to 2% and 28% obtained for H_2O_2 and Fe^{2+} alone, respectively.

BEC technology was recently utilized to power peroxicoagulation process for the removal of RhB dye solution using iron plate as the sacrificial anode and graphite felt cathode (Fig. 6) [171]. The Fe^{2+} is released into the solution by the sacrificial iron anode in peroxicoagulation, which serves as the system's soluble Fe^{2+} source. The Fe^{2+} catalyze the EF process by activation of H_2O_2 to $^{\bullet}OH$ and at high pH, drives the electrocoagulation process. Thus, in peroxicoagulation both EF degradation and electrocoagulation occurs simultaneously at appropriate pH condition [172]. The BEC using diary wastewater performed better compared to municipal and cassava wastewater, achieving 5.23 mA maximum current output and 94% COD removal after 7 days of treatment. The external peroxicoagulation reactor powered by BEC was able to achieve 98% decolorization of the dye solution at the same time.

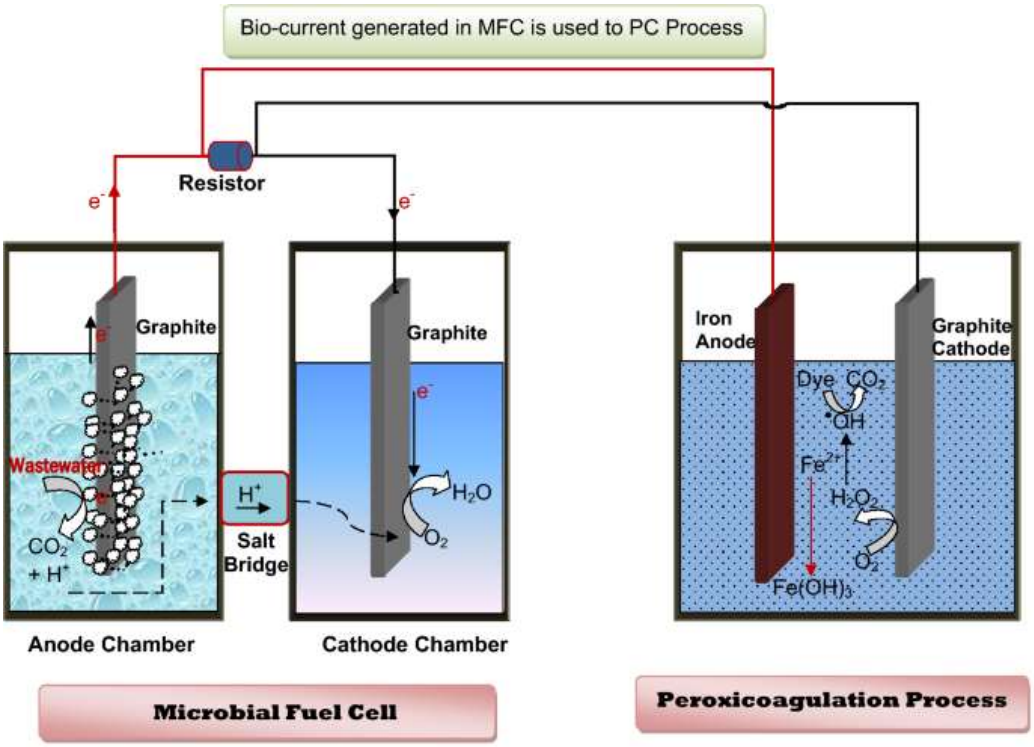

Fig. 6. Schematic of BEC powered external peroxicoagulation reactor. (Reprinted with the permission of ref. [171], Copyright © 2019, Springer-Verlag GmbH Germany)

7.5. BEC combined with indirect EO, or anodic oxidation

BEC system coupled with anodic oxidation/indirect electrooxidation or BEC-powered external electrooxidation (EO) reactor are rarely studied in literature because in the anodic chamber the microbial growth and degradation of organics is predominant. Additionally, since no external electricity supply to the BEC, there is no current to activate the anode and cause the anodic reaction to generate reactive species [131]. Regarding powering the external EO reactor by BEC, the system's output is generally low for most electrodes used in EO. Indeed, the maximum voltage output of most BECs that have been reported in literatures are in the milli-volt range (< 2 V) [132]. This voltage is far lower compared to the oxygen evolution reaction (OER) of most electrode materials applied in electrooxidation wastewater treatment. For example, the OEP of active anode materials such as graphite, platinum, dimensional stable

anode – RuO_2, and IrO_2 are 1.7, 1.6, 1.47 and 1.52 V, respectively, vs SHE in 0.5 M H_2SO_4 [173,174]. Additionally, non-active anode materials, including doped tin oxide, lead oxide, substoichiometric TiO_2 and boron-doped diamond electrodes, which are the best electrode materials for anodic oxidation have higher OER compared to the active anode (1.9 V for doped Tin and Lead oxide, 1.53 for substoichiometric TiO_2 and 2.3 for BDD anode [173,175], thus cannot be powered by the merger voltage generated by the BEC technologies. However, two BEC systems connected in series with an accumulated power output of 900 mV was utilized to drive an external EO reactor for the degradation of Methyl Orange [176]. The ex-reactor equipped with different electrodes (carbon felt, carbon paper, and carbon cloth) was continuously aerated to ensure stable H_2O_2. The dye degradation efficiency of 23%, 76.5% and 90.4% was achieved after 360 min of treatment for carbon cloth, carbon paper and carbon-felt, respectively. The higher degradation efficiency observed with carbon felt and paper was attributed to their high potential for the production of larger quantities of H_2O_2, which contributed majorly to the degradation of the dye. A similar result was obtained using a single BEC system-powered external EO reactor equipped with carbon-felt electrodes [177].

8. Challenges in scaling-up of the coupled system

As it is the case for any electrochemical system, reactor design in bioelectrochemical processes is essential for large-scale applications. MFC and MEC are the most studied and mature bioelectrochemical systems to date, for which, some pilot-scale systems have been developed. Nonetheless, scale-up remains a big challenge for bioelectrochemical processes. Parallel plate reactors have been the most common approach for bioelectrochemical systems [128,178,179]. They include plate-in-tank arrangement and filter press configuration. Such cells are easy to manufacture and operate. Moreover, parallel plate configurations allow for a symmetric current distribution and optimal use of the electrode surface area. Cells with

concentric cylinders are another type of design commonly used in bioelectrochemical reactors. Such systems permit the implementation of large electrode surface areas with more compact designs and minimal dead space, even though electrode maintenance is difficult in these types of stacked arrangements [180]. Moreover, tubular designs require bigger membranes which can be a cost limitation. In general, bioelectrochemical reactors (as well as other electrochemical systems) are modular systems composed of small to medium units, which are connected either in series or parallel according to the treatment capacity. It has been reported that parallel connections achieved long-term and stable power generation without electric failures, while series connections have been reported to entail potential reversal issues [181]. The electrical connections and hydraulics of such modular bioreactors need to be optimized for proper operation, and it represents a current challenge for the development of large-scale systems. The membrane separating the anodic and cathodic compartments is an important component, posing a challenge for larger-scale bioreactors. Membranes are expensive and are subjected to fouling [182–184]. Research on membrane technology is then critical to develop industrial-scale bioelectrochemical reactors. The development of low cost and self-cleaning membranes will facilitate scale-up and field application of bioelectrochemical reactors.

Electrodes are basic elements of electrochemical systems. Accordingly, reactor design must consider the accommodation of electrodes with the highest surface area for biofilm formation at the anode on one hand, and specific electrochemical reactions at the cathode on the other hand. In the case of the anode, 2-D carbon materials in the form of plates, cloths or felts have been the preferred option [185]. Such materials are preferable for parallel plate and tubular reactors. 3-D-configuration electrodes such as carbon brush, carbon sponge and activated carbon have also been utilized, the main issue has been non-uniform current distribution, and scale-up difficulties due to their varied geometries.

The highest-capacity MEC that has been reported was a 1000 L-capacity continuous flow bioelectrochemical cell equipped with 24 electrode modules each one containing six anodes (carbon fiber brush) and six cathodes (stainless steel). This MEF was used to treat winery wastewater with simultaneous electricity generation [186]. Another work operated a 300-L-capacity MFC system for organic carbon removal from urine that contained 12 MFC modules with a total of 432 MFC units. The anodes were carbon fibers wrapped in ceramic cylinder support. The cathodes were activated carbon sheets placed inside the ceramic cylinder [187]. As such, large-scale MEC are limited in literature and extensive research works are require in this area.

In the case of coupled bioelectrochemical systems for anodic energy production and cathodic physicochemical wastewater treatment, the development of large-scale reactors must follow the trends for MFC and MEC mentioned above. Additionally, separating the anodic and cathodic compartments is of primordial importance since the chemical processes with specific experimental conditions in the cathode chamber are not compatible with the microbial anode chamber [128,185]. For example, when combining an MFC with cathodic EF (microbial-EF), the EF half-cell may require acidic pH values to operate, which are detrimental to the biofilm on the anode if the bio-cell is not divided. Besides, the strong oxidants formed during EF are harmful to the microorganisms driving energy production. Finally, more research is needed in the development of pilot-scale coupled bioelectrochemical systems since most reports on such processes involve lab-scale reactors with capacities rarely exceeding 1 L of working wastewater volume.

9. Future perspectives on the development of BEC technology

Environmental destruction and energy shortages are two of humanity's most pressing global problems. Waste biorefinery, pollution mitigation, carbon dioxide reduction and recycling, and the production of green and renewable energy or commercially viable chemicals are all areas where the BEC platform shows great potential in the future. Thus, this technique may provide an alternative to conventional waste biorefinery practices. However, despite its promising advantages and prospects, BEC is still in its early stages of development and has a long way to go before it can be implemented in any meaningful way. Scaling and real deployments of BEC are not even possible unless several hurdles are cleared. By increasing power yields and expanding product options, synthetic biology has the potential to improve the commercial viability of BEC immediately. Synthetic biology will pave the way for medium to long-term bioelectronics and artificial biological materials. We also need to improve our knowledge of the underlying design principles for cellular or secretory extracellular electron transfer component expression. As data analysis and engineering tools advance, researchers will be able to achieve exponential advances in developing these technologies. In the future, researchers will hopefully be able to determine the catalytic effects of EAB and increase the efficiency of direct electron transfer between EAB and electrodes.

10. Conclusions

Renewable energy driving electrochemical systems for wastewater and resources recovery is an exciting and emerging field with huge potential of simultaneously solving environmental pollution and energy demands, two of the key challenges of this century. Bioelectrochemical systems are green energy that generates electricity from waste and have found application in wastewater treatment and value-added products recovery. Microbial and enzymatic electrochemical systems are the two most common classes of BEC which uses microorganisms and enzymes as catalysts for organic carbon conversion, respectively. Energy production in BEC is primarily by either the native respiration chain of EAB which continually obtain energy

by decomposing organic compounds for their cell growth and metabolic functions or electrons transferred by ATP via the discharge of a proton from a cathode into such an intracellular compartment, together with the movement of electrons. The energy production of the BEC is affected by parameters such as electrode materials, microbial metabolism and cell potential, substrate, salinity, and biofilm redox properties.

The energy of BECs is capable of powering different electrochemical wastewater treatments, including MEC coupled with electrosorption, capacitive deionization, electrocoagulation, EF, and anodic oxidation. BEC coupled with EF with *in-situ* or *ex-situ* configurations are the most extensively studied coupled technology because of enhanced energy generation and the excellent performance of the coupled EF treatment. Both homogeneous and heterogeneous EF using Fe^{2+} and iron-bearing solids/modified cathode coupled BECs were effective for degradation and mineralization of different classes of pollutants due to the large quantity of reactive oxygen species ($^{\bullet}OH$) generated by the activation of H_2O_2 by the Fe^{2+}/iron catalysts. Heterogeneous EF coupled BECs has added advantage of being recyclable and effective over a wide pH window. Due to the low electricity output of BECs and relatively high energy demand of anodic oxidation wastewater treatment, BECs coupled with anodic oxidation are less investigated in the literature.

The challenges in scaling-up of couple BECs are related to the BECs reactor designs with electrode configurations such as parallel plates, concentric cylinders and tubular reactors has limitation of large dead space, difficult maintenance of electrodes in stack arrangement and bigger membrane requirements, respectively. Possible potential reversal is a common in stacked cells of BECs which need to be addressed, while the fouling of membrane and its cost is still a key challenge in scale-up this technology.

The biggest disadvantages of the BEC-electrochemical wastewater treatment is the low energy output of the BEC systems which limited the capacity of the electrochemical reactors

that can be operated by this system and lower the removal efficiency of persistent organic pollutants by the couple systems.

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Conflict of Interest

The author declares no conflict of interest.

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