Microbial electro-Fenton: An emerging and energy-efficient platform for environmental remediation

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**HIGHLIGHTS**
- Contemporary developments in the application of MEF systems are elucidated.
- Factors influencing the MEF systems are presented.
- The limitations and future research trends of the MEF are discussed.

**GRAPHICAL ABSTRACT**

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**ABSTRACT**

Environmental pollution and energy are interlinked; thereby an integrated approach is needed based on intra- and cross-disciplinary solutions. Microbial electro-Fenton, an innovative form of microbial electrochemical technologies, is an essential approach in this regard, which couples waste bioremediation and pollutant removal simultaneously from anode and cathode chambers with bioelectricity production. This article reviews the application of microbial electro-Fenton systems for environmental remediation and clean energy generation. Recent advances in fabrication of electrode materials to increase anodic biocompatibility and cathodic oxygen reduction reaction, cell design/configuration, membranes/separators and iron species as Fenton catalysts are discussed in detail. In addition, contemporary developments in the application of microbial electro-Fenton systems to deal with real wastewaters, wide variety of industrial pollutants and various classes of emerging contaminants are elucidated. Furthermore, the limitations and future perspectives are pointed out in detail. We believe that this in-depth review may aid as a reference guide for environmental scientists working on microbial electro-Fenton system.

1. Introduction

Environmental pollution and energy crisis are leading global issues, which are highly intertwined in the networks of human and ecosystems. Struggles in one discipline without considering broader links and concerns often corroborate to be unsound when stimulating sustainability. For example, the huge energy consumption may lead to potential environmental pollution and ecosystem degradation. An integrated approach is essential based on application of intra- and cross-disciplinary solutions [1]. One useful approach to generate bioenergy...
from organic matter (waste stream) is microbial electrochemical technologies (METs), which include microbial fuel cells (MFCs) and microbial electrolysis cells (MECs), novel green technologies for wastewater treatment that generates electricity and hydrogen (H₂) gas as alternate energy, respectively. METs have been extensively applied on biomass-derived waste, wastewater, soil, active sludge, natural water environment, sediments and algae for bioremediation and concomitant bioelectricity/bioenergy production [2–7].

Conventional biological treatment methods have shown adequate outcome in terms of bioremediation but hindered due to the presence of certain bio-recalcitrant compounds. Likewise, physicochemical techniques such as membrane separation, air stripping, coagulation-flocculation etc. are considered to be efficient approaches, but often costly in terms of initial plant outlet, energy demands and recurrent use of chemicals [8]. Advanced oxidation processes (AOPs), which are oxidation methods relying on the combination of strong oxidants (e.g. ozone, hydrogen peroxide, persulfate), ultraviolet irradiation, ultrasound, catalysts (e.g. Fe²⁺) and photocatalyst such as titanium dioxide (TiO₂) to produce hydroxyl radicals (HO•), have emerged as effective water treatment technologies [8–10]. Although AOPs lead to high capital and operating costs and reduced efficacy in natural waters due to HO• scavenging, they are more often being employed owing to the ability of HO• to degrade biorecalcitrant pollutants [11].

Over the last two decades, electrochemical AOPs (EAOPs) have appeared as promising techniques for the destruction of bio-refractory and complex compounds. In such processes, HO• are formed through the oxidation of water on the anode surface (eq. (1)) or via chemical reactions promoted by electrochemically generated species like in the case of the electro-Fenton (EF) process.

\[ \text{H}_2\text{O} \rightarrow \text{HO}• + \text{H}^+ + e^- \]  \hspace{1cm} (1)

EF is one of the most applied EAOPs, and has been widely investigated for the degradation of organic and bio-recalcitrant contaminants present in wastewaters. The conventional EF process is characterized by the electrochemically and in-situ production of hydrogen peroxide (H₂O₂) on the cathode (eq. (2)). It is further dissociated into highly oxidative HO• by Fe²⁺ catalyst (Fenton’s reaction), Fe²⁺ being continuously electro-regenerated at the cathode [12,13]. The main reaction(s) involved in EF is/are depicted in eq. (2) and Fig. 1.

\[ \text{H}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (2)

In the EF process, the operating conditions such as Fe²⁺ concentration, applied current, electrolyte, pH and temperature impart significant effect on the efficiency of the process [14]. It has more advantages than conventional chemical Fenton process or other EAOPs owing to the high efficacy of the Fenton reagent’s (H₂O₂ and Fe²⁺) that is continuously electro-generated and the saving of chemical storage and transportation costs [15]. Despite all these advantages, the electric energy demand to execute the process via EF or photo-EF limits its large-scale application. For instance, the electrical consumption of the EF in wastewater treatment can reach 19 kWh m⁻³ or 530 kWh kg⁻¹ TOC (total organic carbon), which is much higher than that for biological treatment processes [12,16].

Recently, METs such as MFCs and MECs have been demonstrated as promising alternatives for in situ H₂O₂ synthesis in the cathode [17–21]. Rozendal et al. [18] investigated that MFCs were capable of generating 1.9 kg H₂O₂ m⁻³ d⁻¹ from acetate substrate, representing a novel alternative to industrial production of H₂O₂. Sim et al. [19] observed the maximum production rate of 141 mg H₂O₂ L⁻¹ h⁻¹ and 6 mg H₂O₂ L⁻¹ h⁻¹ in the MEC fed with acetate and wastewater, respectively. Applying an external optimum voltage of 0.4 V to a MFC achieved 705.6 mg H₂O₂ L⁻¹ at a production rate of 2.12 kg m⁻³ d⁻¹ with energy input of 0.66 kWh kg⁻¹ H₂O₂ [20]. On the basis of these investigations, instead of only H₂O₂ production, the cathodic EF process coupled to MFC was developed to initiate the Fenton’s reaction supplementing an iron source. The pioneering investigation in this regard was carried out in 2009 by Zhu and Ni [22]. As shown in Fig. 2, a burgeoning research is being carried out in this area, applying this novel technology for environmental remediation coupled with electricity production.

In the MFC-driven EF process, namely microbial electro-Fenton (MEF) system, which is also named as bioelectro-Fenton (BEF) process in some studies, H₂O₂ is produced in-situ in the cathode chamber by coupling anodic oxidation of organic compounds (energy production), thereby no external energy input is needed as opposed to the conventional EF or photo-EF techniques. The produced H₂O₂ produces HO• radical by the external addition of Fe²⁺ (Fenton’s reaction) or Fe³⁺ (Fenton-like reaction), which oxidize the biorefractory organics. The mechanism of MEF is represented in Fig. 3 (b) and detailed in subsection 2.3.

Unlike conventional METs, MEF systems could efficiently remove organic pollutants from anode and cathode chambers simultaneously [22–24]. This process has been applied to deal with wide range of complex wastewaters [23–27], emerging contaminants [22,28–33] and industrial dyes like azo-dyes [15,34,35], Congo Red [36], Methylene Blue [37], Acid Orange 7 (AO7) [38] etc. Here we review the application of MEF processes for environmental remediation and energy generation. We first describe the mechanisms and fundamentals of MEF systems. Next, we elucidate the influence of the different parameters affecting the overall efficiency in terms of pollutants removal. Finally, we discuss the limitations and the challenges for future research. We believe that this in-depth review will aid as a reference guide for environmental scientists working on MET and MEF systems, and the contextual facts will give assistance in driving further advances on viable solutions for environmental remediation.

2. MEF fundamentals

2.1. Anodic reactions

As shown in Fig. 3 (a), in a typical MEF system, the electroactive bacteria oxidize the organic matter in the anode chamber and release electrons obtained from an electron donor (either simple substrates or complex wastewaters) to the anode (negative terminal). This occurs either through direct contact, nanowires, or mobile electron shuttles [39,40]. This aspect has been explained in section 4.2. During electron production, protons are also produced in excess, which migrate through the ion exchange membrane (IEM) into the cathode chamber. Mostly, the number of generated protons is equal to the number of transferred electrons, as shown for the bioelectrocatalytic oxidation of carbohydrates, hydrocarbons, and hydrogen at the anode (eq. (3)).
The substrate oxidation reactions in the anode chamber of MET are expressed in eqs. (4–7).

**Acetate oxidation reaction:**
\[
\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8e^- \quad (4)
\]

**Glucose oxidation reaction:**
\[
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 24\text{H}^+ + 24e^- \quad (5)
\]

**Propionate oxidation reaction:**
\[
\text{CH}_3\text{CH}_2\text{COOH} + 4\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 14\text{H}^+ + 14e^- \quad (6)
\]

**Butyrate oxidation reaction:**
\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + 6\text{H}_2\text{O} \rightarrow 4\text{CO}_2 + 20\text{H}^+ + 20e^- \quad (7)
\]

### 2.2. Cathodic reactions

#### 2.2.1. Four-electron reduction to H\(_2\)O (MFC)

The electrons flow from the anode through an external resistance (or load) to the cathode where they reduce oxygen (terminal electron acceptor) to water by four-electrons reduction (eq. (8)) [41], thereby generate bioelectricity.

\[
\text{O}_2 + 4(\text{H}^+ + e^-) \rightarrow 2\text{H}_2\text{O} \quad (8)
\]

The full reduction of O\(_2\) to H\(_2\)O involves four reduction steps having three different intermediates i.e. ’OOH, ’O and ’OH, as specified in eq. (9) [42].

\[
\text{O}_2 + 4(\text{H}^+ + e^-) \rightarrow ’\text{OOH} + 3(\text{H}^+ + e^-) \rightarrow ’\text{O} + 2(\text{H}^+ + e^-) \rightarrow ’\text{OH} + (\text{H}^+ + e^-) \rightarrow 2\text{H}_2\text{O} \quad (9)
\]

#### 2.2.2. Two-electron reduction to H\(_2\)O\(_2\) (MEF)

As Fig. 3 (b) demonstrates, in MEF system, the exoelectrogenic bacteria are used in the anode chamber as catalyst to oxidize organic content in waste stream and produce H\(_2\)O\(_2\) in the cathode chamber by two-electron partial reduction pathway (eq. (10)).

\[
\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad (10)
\]

Theoretically, the synthesis of H\(_2\)O\(_2\) by MEF system is possible, since the cathode potential for two-electron oxygen reduction reaction, ORR i.e. \(~0.260\text{V vs. SHE}\) [43] is higher than the anode potential (\(~0.524\text{V vs. SHE}\)) [44]. Depending on the electrocatalytic properties of the cathode materials, both the two- and four-electron oxygen reduction pathways are possible. The production of H\(_2\)O\(_2\) via partial reduction of O\(_2\) only involves hydroperoxyl radical (’OOH) as a reaction intermediate (eq. (11)).

\[
\text{O}_2 + 2(\text{H}^+ + e^-) \rightarrow ’\text{OOH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}_2 \quad (11)
\]

Classically, both associative and dissociative pathways are considered, depending upon whether the oxygen molecule dissociates before reduction. The associative pathway contains three different intermediates as mentioned in eq. (9), dissociative pathway only involves two different intermediates, i.e. ’O and ’OH (eq. (12)) [42].

\[
\frac{1}{2}\text{O}_2 + 2(\text{H}^+ + e^-) \rightarrow ’\text{O} + 2(\text{H}^+ + e^-) \rightarrow ’\text{OH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}_2 \quad (12)
\]

Although the two-electron pathway is considered undesirable in fuel cell applications, as it lowers its efficiency and often affects the stability of the proton-exchange membrane (PEM) [45]. However, electrochemical H\(_2\)O\(_2\) synthesis is an emerging alternative for onsite applications in the pulp and paper, textile, synthetic chemical and wastewater treatment industries. The capability of a fuel cell to both produce H\(_2\)O\(_2\) and harness energy would be a major step toward sustainable green chemistry and a striking substitute to the conventional anthraquinone-based H\(_2\)O\(_2\) synthesis method [46,47].

### 2.3. Fenton’s reaction

During MEF processes, H\(_2\)O\(_2\) is generated \textit{in situ} in the cathode chamber, which is a strong oxidizing agent (E\(_\text{°}\) = 1.8 V), and capable of degrading biorecalcitrant organic compounds. In order to introduce Fenton’s reaction, iron source as Fenton catalyst is dosed which reacts with the \textit{in situ} generated H\(_2\)O\(_2\) and results in ’OH formation (E\(_\text{°}\) = 2.8 V) as represented in Fig. 3(b) and eq. (13). The ’OH can remove refractory pollutants (RP) converting them to simpler oxidation products (eq. (14)).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + ’\text{OH} + \text{H}_2\text{O}, \text{k} = 63\text{M}^{-1}\text{s}^{-1} \quad (13)
\]

\[
’\text{OH} + \text{RP} \rightarrow \text{oxidation products (CO}_2, \text{H}_2\text{O)} \quad (14)
\]

Other reactions also occur in MEF reactor, such as oxidation of Fe\(^{3+}\) to Fe\(^{4+}\) by O\(_2\) (eq. (15)) and reduction of Fe\(^{1+}\) to Fe\(^{2+}\) (eq. (16)). Some of the Fe\(^{3+}\) produced as a result of Fenton reaction (eq. (13)) might be reduced to Fe\(^{2+}\) through eq. (17), however the rate is several order slower than the Fe\(^{2+}\) to Fe\(^{3+}\) conversion through eq. (13). In MEF process, Fe\(^{2+}\) could be enhanced by introducing bio-electrons into the
Fe²⁺/Fe³⁺ redox cycle regeneration and thus stimulate the Fenton’s chain reaction efficacy [30].

\[
\begin{align*}
\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ & \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + '\text{OOH} + \text{H}^+, k = 0.002-0.01 \text{ M}^{-1}\text{s}^{-1}
\end{align*}
\]

3. Evaluations of MEF systems

Since MEF is a MET-driven process, all the computations employed in MFCs (eqs. (18)–(31)) can be applied in MEF systems as well. The electrochemical evaluation of MEF systems can be acknowledged by their resultant voltage, current, power output as well as coulombic efficiency (CE) etc., discussed in the following text.

Power generation is the main goal of MFC operation, and it is the product of the measured voltage \(U\) and current \(I\) calculated as

\[
P = I \times U
\]

The current produced in the system is calculated by measuring the voltage \(U\) across the load or external resistor \(R_{\text{ext}}\) (eq. (19)), hence power output can be computed according to eqs. (20 or 21)

\[
I = \frac{U}{R_{\text{ext}}}
\]

\[
P = \frac{U^2}{R_{\text{ext}}}
\]
The power output normalized to surface area of electrode and electrolyte volume can be calculated according to eqs. (22) and (23), respectively.

\[ P = \frac{I^2 \times R_{cat}}{A \times R_{cat}} \]  

(21)

where, \( A \) is the surface area of electrode in cm\(^2\) or m\(^2\), and \( V \) is electrolyte volume in m\(^3\).

Beside power output in METs, we also seek to extract as much electrons stored in the biomass/carbon source as possible, and to harness as much energy as possible from the system. The recovery of electrons is referred to as coulombic efficiency (CE); defined as the ratio of coulombs (electrons) recovered as current to that in the starting substrate. CE can be computed using eqs. (24–27) depending on the substrate nature and operation mode.

\[ CE(\%) = \frac{M \int_{t_0}^{t} Idt}{Fbq \Delta C} \times 100 \text{ (Simple substrate, fed – batch system)} \]  

where, \( \Delta C \) is the simple substrate concentration change (mg L\(^{-1}\)) over the batch cycle to completion over time, \( t \) (s), \( M \) is the molar mass of the substrate (g mol\(^{-1}\)), \( I \) is current generated during whole batch cycle (A), \( b \) = number of moles of electrons per moles of COD (4 mol e\(^-\) mol\(^{-1}\) COD), \( F \) is Faraday’s constant (96,480 C mol\(^{-1}\)), \( V_{cell} \) is anolyte volume (L)

\[ CE(\%) = \frac{M \int_{t_0}^{t} Idt}{Fq \Delta C} \times 100 \text{ (Simple substrate, continuous system)} \]  

(25)

where \( q \) is influent flow rate (L s\(^{-1}\))

\[ CE(\%) = \frac{M I_{cell}}{Fq 4 \Delta COD} \times 100 \text{ (Complex substrate, continuous system)} \]  

\[ M \text{ for complex substrates is the molar mass of O}_2 (32 \text{ g mol}^{-1}) \]

Faradic efficiency, defined as cathodic H\(_2\)O\(_2\) production divided by the charge production, is calculated according to eq. (28)

\[ \text{Faradic efficiency (FE, \%) } = \frac{nFCH_2O_2V}{\int_{t_0}^{t} Idt} \times 100 \]  

(28)

where, \( n \) represents the stoichiometric number of electrons transferred in reaction (\( n = 2 \)), \( F \) = Faraday’s constant (96,480 C mol\(^{-1}\) e\(^-\)), \( C_{H_2O_2} \) = measured concentration of H\(_2\)O\(_2\) (mg L\(^{-1}\)), \( V \) = (catholyte volume (mL)).

The most notable feature of MET systems is the internal resistance. The least internal resistance of a MET system means an efficient performance. Internal resistance is concomitant with ohmic losses (\( R_o \)), activation losses (\( R_a \)) and mass transfer losses (\( R_{mt} \)), eq. (29). The most preferred methods to evaluate the internal resistance is electrochemical impedance spectroscopy (EIS) using a Nyquist plot by a potentiotstat. Polarization slope and power density peak methods are also the simplest and quick ways in this regard [44].

\[ R_{int} = R_o + R_a + R_{mt} \]  

(29)

The energy conversion recovery (\( \varepsilon_E \)) can be calculated as the ratio of power produced by the cell over a time interval \( t \) to the energy content of the COD consumed. The energy conversion efficiency is given using eq. (30):

\[ \varepsilon_E(\%) = \frac{M \int_{t_0}^{t} E_{cell}Idt}{\Delta H_{fuel} \times 100} \]  

(30)

where, \( E_{cell} \) is the measured cell voltage (V), \( \Delta H_{fuel} \) is the heat of combustion values for wastewater calculated from the COD and the amount of COD consumed (g).

The potential difference across the membrane because of concentration gradients between the anode and cathode should be considered. Generally, this potential gradient can be computed for electrolytes of various compositions based on the Goldman–Hodgkin–Katz equation (eq. (31)):

\[ E = \frac{RT}{2F} \ln \left( \frac{\sum a_i}{\sum a_f} \right) \]  

(31)

where \( a_i \) and \( a_f \) are the activities of the ionic species in compartments I and II, respectively. \( R \) is the universal gas constant (8.314 J K\(^{-1}\).mol\(^{-1}\)), \( T \) is the absolute temperature (K), \( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)).

Proton transfer via electric migration in an electric field can be defined through the transference number of proton (\( t_p \)) or the fraction of the total current that proton carries, and can be computed as:

\[ t_p = \frac{\zeta \lambda_p}{\sum \zeta_i \lambda_i} \]  

(32)

where, \( \zeta_p \) and \( \zeta_i \) are the concentrations of proton and ion \( i \), respectively, and \( \lambda_p \) and \( \lambda_i \) are the molar ionic conductivities for proton and ion \( i \), respectively.

Ammonium ions (NH\(_4^+\)) crossover through cationic exchange membrane (CEM) is a common phenomenon which sometimes creates hindrance in the cathodic reactions, and can be estimated by eq. (33):

\[ W = \sum \frac{C_i V_i}{M_i} \]  

(33)

where, \( W \) is NH\(_4^+\) mass (mmol), \( C_i \) and \( V_i \) represent NH\(_4^+\) concentration (mg-N L\(^{-1}\)) and catholyte (L) at time \( t \), and \( M_i \) is molar mass of nitrogen (14 g mol\(^{-1}\)).

4. Configurations of MEF system

4.1. Reactor designs

Various types of reactor designs have been employed in MEF related studies. Fig. 4 presents the representative configurations of cells used in MEF systems. Dual chambered configuration either H-type bottle reactors or rectangular reactors, made up of various materials such as glass, Plexiglas, polymethyl methacrylate or polycarbonate sheets, is the most common design of MEF systems. The anode and cathode are separated by ionic exchange membranes/separators such as cationic exchange membrane (CEM) [23,24,48], proton exchange membrane (PEM)-Nafion\(^®\) [25,37,49,50], anionic exchange membrane (AEM) [51], bipolar membrane [26,37,52], Gore-Tec\(^®\) cloth [27,34] or salt bridge [53] (more details are given in section 4.5). The distance between the anode and the cathode in such setups are reported to be 3–7 cm, having a broader range effective volume of 64–1500 mL for each chamber. Bottle reactors are the most conventional dual-chambered set up in MET reports (Fig. 4-a). Such reactors have wider electrode distance (c.a. ≥ 5 cm) and smaller membrane surface area corresponding to cell volume, which sometimes may hinder the overall performance due to the great ohmic resistance that develops in the system. As shown in Fig. 4-b, Birjandi and colleagues [25,50] constructed MEF reactors with two rectangular chambers of the same size separated by a PEM. 84.02% of COD removal was achieved in the cathodic chamber in 50 h, while 8.05% of COD was removed in the anode compartment during the treatment of landfill leachate [25]. Such reactors are either cube-shaped or rectangular shaped with varying
sizes. These kinds of reactors are easy to construct and simple to operate; however, agitation is needed depending on the size of the reactor to homogenize the solution in the chambers. Cylindrical-shaped reactors were also applied for MEF systems (Fig. 4-c) covering the inner chamber by membrane to separate anode and cathode [27], however solution mix up using magnetic stirrer in lab-scale experiments is not favorable with such arrangements, and use of electric peristaltic pumps for homogeneity may increase the electric energy consumption. For the cylindrical reactor, a maximum of 35.2% and 57.3% of COD and TOC removal, respectively, was achieved in the cathode compartment (46.6% of COD removal and 38.4% of TOC removal in the anode chamber) when treating swine wastewater (hydraulic retention time of 0.36 d). This represented an overall of 76.7% and 95.7% of COD and TOC removal: the effluent was first treated in the anodic anode chamber and transferred to the cathode chamber for afterwards. The dual-chambered reactors are easy to construct and operate, separating two different conditions, such as biotic anolyte with abiotic neutral, alkaline, or acidic pH (pH 2–4) catholyte. However, the use of membranes/separators makes this configuration less economical and practical for scale up operations. Thus, a modified type of MEF system...
was devised by Zhu and Logan [33], where the Fenton reagent (Fe\(^{2+}\)) was released from a sacrificial iron anode in an undivided electrocatalytic cell that was powered by an isolated single chambered air-cathode MFC (Fig. 4-d). No membrane is needed for this system. Total phenol removal was achieved in this system, with 75% of TOC decrease following 22 h of treatment. This kind of configuration can be regarded as a conventional EF system powered by the energy generated by MFC. Thus, it is limited by the current development of MFCs for electricity production. Liu and co-researchers developed an “anodic Fenton” (AFT) system for energy-efficient treatment of the dye acid orange 7 (A07) [38]. As shown in Fig. 4-e, this system was composed of a divided AFT reactor and dual-chambered air-cathode MFC. The proposed system degraded organic substrate in the MFC anode chamber, which was connected to the cathode chamber of the AFT system. A07 degradation occurred in the AFT anode chamber, where the Fenton’s reaction was promoted by the dissolution of a Fe electrode and the external injection of \(H_2O_2\). The dye was degraded by 87% in the anodic AFT chamber in 15 min of treatment (the COD and TOC removals were not evaluated). Besides the fact that \(H_2O_2\) was not produced by the electrochemical reduction of \(O_2\), the main issue of this system is the use of two divided cells (elevated resistance), which represents the need of two membranes, in addition to the cost of \(H_2O_2\).

Some investigations developed hybrid MEF configurations. Recently, microbial reverse electrodialysis electrolysis cell (MREC)-based Fenton system was proposed that consisted of anode and cathode chamber separated by a reverse electrodialysis (RED) stack [51]. In the MREC-Fenton integrated system, \(H_2O_2\) synthesis was driven by the electrons produced from both the electrogenic bacteria in the anode and salinity-gradient between sea water and fresh water in the RED stack. The system (with a capacity of only 40 mL) achieved more than 90% of degradation of the dye orange G and 99.6% of TOC removal in 5 h treatment under optimal conditions (pH 2), while the COD removal in the anodic chamber was 81%. Fernandez de Dios et al. [53] developed a hybrid cell that consisted of a sediment microbial fuel cell (SMFC) with an electro-Fenton cathode cell. The electro-Fenton cathode was connected to the anode chamber through a salt bridge. This system was evaluated for the degradation of different dyes (lissamine green B, crystal violet, indigo carmine, reactive black 5, poly R-478), which were almost totally degraded following 15 min of treatment, except for poly R-478 which was only removed by 19.1% in 60 min. The setup consisted of a basic two dived electrolytic cell separated by a salt bridge, with a treating volume of 0.15 L in the cathode chamber. The COD and TOC decays were not investigated.

Even if promising results have been obtained so far, current configurations need to be improved in order to increase the electrical output and removal efficiencies during shorter treatment times, in addition to the capacity to treat higher organic loads (most MEF systems have been tested with low pollutant concentration generally below 100 mg L\(^{-1}\)). Accordingly, further research needs to be conducted aiming at the development of cost effective, efficient and scalable configurations. This point is further discussed in the section 8 of this review.

### 4.2. Electrogenic biofilm

In METs, microorganisms that are capable of exocellular electron transfer (EET) have been described in literature with various terms such as electrogenic bacteria, electrochemically active bacteria (EAB), anode respiring bacteria (ARB), exoelectrogens and electrogenerics [5,54-56]. Among electrochemically active bacteria, \textit{Geobacter} and \textit{Shewanella} spp. are examples of well studies model ‘exoelectrogens’ providing direct ET (DET) via c-type cytochromes located on the outer membrane [39]. Other electrogenic bacterial species in mixed culture e.g., \textit{Comamonas, Arcobacter, Dechloromonas, Clostridium, Spingobacterium, Paludibacter} etc. [57] attach to the anode surface and form a thick biofilm (Fig. 3). The developed biofilms have a live outer-layer and a dead inner-core. Thick formation of biofilm sometimes hinders the EET. Thereby an optimum biofilm deposition is appropriate for current generation. The EET rate in different METs fundamentally depends on the electrochemical behavior of anode biofilm according to Gibbs free energy. Bioelectroactive organelles such as outer membrane cytochromes, conductivity pilii and extracellular excretions have a critical role on the EET between the ARB biofilm and the anode surface [58,59]. Several reviews have explained the underlying reasons for EET, including cellular respiration and possible cell to cell communication [39,40,56].

Both pure and mixed cultures have been employed in METs. The most studied microbes are \textit{Geobacter} and \textit{Shewenella}, which gave better results when inoculated as pure cultures [60]. However, the average current and maximum power output from mixed bacterial consortia were higher than pure cultures [56,61]. Moreover, compared to pure cultures, enriched microbial consortia were more stable and robust owing to nutrient adaptability and resistance to stresses [61]. Electrogenic bacteria in mixed culture are > 15% of total microbial consortia, which involve in power production process in METs [5]. Further research is needed to explore the behavior of electroactive biofilm and discover new electrogenic species among the anodic microbiome.

### 4.3. Anode materials

The anodic chamber contains microorganisms responsible for the production of the electrons that migrate to the cathode for the reduction of \(O_2\) into \(H_2O_2\) (eq. (10)). Microorganisms adhere on the anode surface where electrons are transferred following substrate oxidation. Electrons transfer can take place directly or indirectly: direct electron transfer occurs through the cell-surface redox-active proteins (e.g., c-type cytochrome), while mediated electron transfer is driven by either secondary or primary metabolites produced by the microorganism [62]. Generally, the electrical current and power output generated from direct electron transfer is lower than that generated from mediated electron transfer [40]. The anode materials need to be biocompatible and non-toxic. Besides, they have to possess high conductivity, stability and surface area, as well as accesible costs. Because carbonaceous electrodes compile with the above mentioned characteristics, they have been the most utilized anodes in METs studies, including MEF [63]. Carbon felt (CF), carbon fibers, graphite and granular graphite are some of the most common anode materials used in MEF (Table 4). In the case of metallic electrodes, iron has been the main choice in MEF cells. A quick inspection of Table 4 shows that CF has been the most used anode for MEF applications. CF is a 3D porous, highly conductive and inexpensive material. Its porous structure confers it a high surface area for biofilm colonization and thus electron transfer [64].

The chemical structure of the anode surface and its morphology play a major role in the interaction between the biofilm and the electrode, since the electron transfer from the microbes to the surface is considered as the limiting step for bioelectricity production [64]. Surface modification and/or activation are trend research topics in METs that are aimed at improving bacterial adhesion and electron transfer. Surface modifications include polymer deposition [65], oxygen or nitrogen doping [64,66], immobilized mediators [67-69], carbon nanoparticles (nanotubes, graphene) [70-72], metal nanoparticles [73] among others [67]. It has been reported that biofilm adhesion is improved in positively charged and hydrophilic surfaces [74,75]. For example, it was found that polypodamine with superhydrophilicity deposited on an activated carbon substrate increased by 31% the maximum power density generated by a MFC (from 613 ± 9 to 803 ± 6 mW m\(^{-2}\)). Moreover, the Columbic efficiency rose from 19% to 48%. It was ascribed to the different functional groups present in polypodamine, such as amine, catechol, quinone, carboxylic acid and indol, which enhanced the electron transfer [74]. In a different investigation, carbon fibers were modified with vertical carbon nanotubes/polyprrole composites, which showed an enhanced conductivity and good biocompatibility.
The generation of electricity was improved by 2.63 times as compared to the unmodified anode, producing a maximum power density of 1876.62 mW m\(^{-2}\) [76]. The increased performance was attributed first, to the improved electrode transfer promoted by the vertically-grown nanotubes and second, to the higher biocompatibility of the poly-pyrrole-coated surface [77]. The use of riboflavin-salicylaldehyde-4-aminosalicylic acid tetra-carboxylate ester as mediator on carbon rods was reported to increase 7 times the power generation as compared to the raw electrode in a microbial solar cell, which reached a maximum power density of 0.847 W m\(^{-2}\). In this case, the excellent redox capabilities of the mediator (specifying the flavin structure) allowed for an improved electron transfer from the biomass to the carbon substrate, thus increasing power generation [68]. Another redox mediator, naphthoquinone polymer NQ-LPEI, which was attached on carbon felt anodes, was reported to shorten the startup time for bacterial colonization and enhance electrochemical communication between the biomass and the anode surface in a MFC. As a result, the power output was increased with respect to the uncoated electrode, reaching 0.53 ± 0.02 W m\(^{-2}\); substrate degradation was also enhanced [78]. In a MEF system, it was found that a CF anode modified with a poly-pyrrole/anthraquinone-2,6-disulfonate (PPy/AQDS) increased the power density of the cell, improving the oxidative ability of the process to degrade and mineralize the dye Orange II [35].

Most of the work on anode modifications has been done for MFC and little attention has been paid on electrode modifications for MEF. Even though the same principles are applicable, more research is needed on anodes modified with nanomaterials and redox mediators to improve the efficiency of MEF systems in pollutant degradation.

### 4.4. Cathode materials

The properties of the cathode material play critical role in the production of H\(_2\)O\(_2\) and consequently in the performance of the MEF system. H\(_2\)O\(_2\) promotes the formation of ‘OH via the well-known Fenton's reaction (eq. (13)), for which Fe\(^{2+}\) ions are needed as catalyst. During the process, Fe\(^{3+}\) ions are constantly regenerated at the cathode via eq. (16) so only small amounts of catalyst are required [12]. Numerous studies have demonstrated the potential of EF to mineralize organic pollutants found in different kinds of wastewater [79-81]. Carbon-based electrodes have been the preferred cathodes including CF [82], carbon sponge [13], reticulated carbon vitreous [83], graphite [84], carbon fibers [85,86], gas diffusion electrodes (GDE) [87], carbon nanotubes [88] and graphene [86,87] etc. The same principle applies to MEF, in which the energy to produce the Fenton's reagent is provided by the active microorganisms in the anodic compartment. Hence, high-surface area CF has been the most employed cathode material in MEF system (Table 4). It is known that CF has good electrocatalytic properties for O\(_2\) reduction via the H\(_2\)O\(_2\) pathway, besides its good mechanical properties, stability and malleability [89].

Structural electrode modifications have been reported for the improvement of the electrocatalytic production of H\(_2\)O\(_2\) in conventional EF, which is a hot topic among the scientific community. Such modifications include chemical treatment to add oxygen- or nitrogen-bearing functional groups [90], polymer deposition [91], nano-zero-valent iron co-doping [92], and synthesis of composite materials incorporating nanomaterials such as carbon black [93], carbon nanotubes [88] and graphene [87]. Accordingly, high production of H\(_2\)O\(_2\) has been achieved, which enhanced EF performance: 832 mg L\(^{-1}\) of H\(_2\)O\(_2\) with carbon black-based, 805 mg L\(^{-1}\) with CNT-based and 495 mg L\(^{-1}\) with graphene-based.

It is worthy of note that all the above-mentioned modified cathodes were used in a GDE configuration, in which the ORR is improved due to the direct flow of O\(_2\) through the electrode's pores in contact with the solution [94]. In the case of MEF systems, it was reported that the use of modified CF electrodes with pyrrole/anthraquinone-2,6-disulfonate by electropolymerization increased the cell's power density by one order of magnitude (823 mW cm\(^{-2}\)) as compared to the raw materials, as well as the cathodic production of H\(_2\)O\(_2\) (2.86 mg L\(^{-1}\) vs 0.63 mg L\(^{-1}\) with unmodified CF). As a result, the oxidative capacity of the MEF treatment of Orange II was enhanced [35]. In an MEF report [92], activated carbon (AC) air cathode was modified by co-pyrolyzing of AC with glucose and doping with nano-zero-valent iron (denoted as nZVI@MAC) to facilitate two-electron ORR and achieved higher oxidizing performance.

Another type of cathode materials that have been used in conventional EF are carbon aerogels (CAs), which are 3D and highly-porous materials that can be easily functionalized accommodating different species within their network [95]. Incorporation of Fe and/or Cu particles has been shown to enhance mechanical and thermal strength of CAs, and these hybrid materials have emerged as potential candidates for heterogeneous EF systems [96,97]. Fe-Cu-C aerogel was successfully used as cathode during the EF treatment of dyeing wastewater, achieving total methylene blue (MB) removal and around 80% of TOC mineralization in pH values ranging from 3 to 9 [98]. Similarly, a macroporous Fe\(_2\)O\(_3\)-carbon aerogel cathode was utilized in the photo-electron-Fenton (PEF) degradation of imidacloprid at neutral pH: total degradation of the insecticide was achieved in 150 min and almost total TOC removal was attained following 8 h of electrolysis [99]. The main limitation of functionalized CAs is their quite complex preparation steps (sol-gel formation, solvent exchange, ambient pressure drying and pyrolysis). All the above-mentioned innovative nanomaterials-based electrodes are potential alternatives to be explored in MEF systems.

The use of composite electrodes loaded with iron catalysts has been a common practice in MEF systems (Table 4). In such heterogeneous systems the oxidant species are formed through two different routes: i) via surface Fenton-like reactions or ii) by release of Fe\(^{2+}\)/Fe\(^{3+}\) ions into the solution which promote the homogeneous Fenton's reaction. This point will be addressed in detail in section 4.6. In fact, it is known that the amount of Fe\(^{2+}\) ions influence the efficiency of the EF process. In conventional EF, Fe\(^{2+}\) ions are generally introduced in the solution to be treated in the form of soluble salts, mainly as FeSO\(_4\). Because of the catalytic cycle established at the cathode (continuous Fe\(^{3+}\) reduction according to eq. (16)), only small Fe\(^{2+}\) amounts are necessary, ranging between 0.1 and 0.5 mM (5.58–27.92 mg L\(^{-1}\)). FeSO\(_4\) has also been the preferred source of Fe\(^{2+}\) in BEF (Table 4). The use of heterogeneous catalysts as source of iron ions is another alternative in conventional EF: heterogeneous EF [100,101]. The catalysts can be particles suspended in the solution (natural minerals or synthetic nanoparticles) or they can be incorporated to the cathode as the above-mentioned composite electrodes.

### 4.5. Membranes

In dual chambered MET/MEF cells, the anode and the cathode must be separated by a membrane in order to avert the short circuit and advance the system performance among other features. The membrane is an important part of METs/MEFs that greatly affects its performance. A wide range of materials have been employed as separators in METs/MEFs such as ion-exchange membranes, glass fibers, porous materials, salt bridge, ceramic-based membranes, graphene-based membranes and composite membranes [53,102-105]. The pros and cons of various membranes employed in METs/MEFs are detailed in Table 1.

Ion exchange membranes include cationic exchange membranes (CEMs), proton exchange membranes (PEMs) and anionic exchange membranes (AEMs). CEMs such as CMI-7000S (Membranes Inc., USA) are frequently used in MET/MEF studies, as they are less costly and often structurally more stable than PEMs (e.g., Nafion 117, 211 or 212), which exhibit proton conductivity. According to Harnisch et al. [106], CEMs reveal comparable cation conductivity and mechanical stability, however exhibit a raising internal resistance compared to Nafion due to transportation of all cations across the membrane. Nafion (PEM) demonstrates greater conductivity to various cations due to the presence
of negatively charged functional groups (i.e. sulfonate SO₃⁻) attached to the fluorocarbon backbone (-CF₂-CF₂) of perfluorosulfonic acid membrane [102,107]. They are more specific and only allow small cations to freely penetrate through it [112]. In terms of power output, PEMs are considered superior to CEMs. However, their high cost is discouraging to scaling up the METs. It has been assessed that the membrane is responsible for roughly 40% of the cost of MFCs [108] considering Nafion-117 as the separator. Furthermore many issues such as significant oxygen and substrate crossovers, transport of cations other than protons and biofouling, are limiting factors for MET/MEF applications [109].

AEMs are polymer electrolytes that transfer anions, such as HO⁻ and Cl⁻, as they contain positively charged cationic groups bound covalently to a polymer backbone [110]. Although AEMs have not been as widely used in MET/MEF processes as CEMs, there were reports that AEMs could function better than CEMs and Nafion [111]. Employing AEMs could aid proton transfer with supplementing phosphate or carbonate buffers, resulting in high voltage output [112]. However, AEMs are more susceptible to deformation [113], which may raise considerable internal resistance [102], an unfavorable phenomenon which exacerbates efficiency of METs; hence they could not be a viable option for long-term operations. In principle, operating the AEM with carbonate ion conduction might be a substitute that would nullify the problem of membrane degradation by OH⁻ ions.

Recently, porous ceramic and clayware membranes have been extensively employed in METs. Chemical, thermal and mechanical stability, low-cost, easy availability and certain other pros make them an alternate for costly polymeric IEMs [114]. Moreover, good power performances in short and long-term periods were observed using ceramic membranes (CMs) [115].

Although the use of ceramics in METs proved to be low cost while improving performance to a greater extent, there are numerous challenges to be addressed through more investigation on ceramic-based MFCs. Most important problem associated with ceramic material as separators include its brittleness and/or mechanical strength.

Recently, a great deal of studies has focused on the synthesis of composite and nano-composite membranes, as they are inexpensive and can produce more power output than existing Nafion membranes. Angioni et al. [116] prepared composite separators based on Polybenzimidazole (PBI). These membranes achieved higher power density (844–1521 mWm⁻²), COD removal rate (7.3–14.3 mgL⁻¹h) and coulombic efficiencies (14–31%) in treating wastewater with respect to Nafion⁺⁺ (129 mW⁻³, 22% and 5.1 mgL⁻¹h, respectively). Moreover, the study claimed that PBI-based membranes were more promising than Nafion⁺⁺ in terms of biofouling issue and cost.

New membrane materials with rapid fabrication processes such as casting and 3D printing have been employed for MFCs [117], which significantly expands the range of possible MFC geometries and improves the ease of fabrication and assembly of multiple units. The use of a 3D printed polymer and a cast latex membrane verified the prospect of rapid, low cost fabrication of MFCs with a considerably more specific ion exchange area than planar membrane materials.

The first attempt to incorporate graphene (Gr) in MFC membrane was made by Khilar et al. [118], who prepared the Gr-modified polyvinyl alcohol silicotungstic acid (PVA-STA) membrane by solution casting for MFCs. Studies with Gr-based membranes revealed higher proton conductivity, mechanical strength and the power output [104]. These outcomes make Gr-based membranes a promising alternative of Nafion for MFCs.

5. Operations of MEF systems

5.1. Iron catalyst

The iron source is one of the key factors to influence the performance of the MEF system. For most applications it does not matter whether Fe²⁺ (Fenton) or Fe³⁺ (Fenton-like) salts are employed as Fenton catalyst. In any case, Fe²⁺ is constantly regenerated at the cathode through the reduction of Fe³⁺. Nevertheless, some differences have been reported in few studies, where Fenton reactions proved better performance than Fenton-like reactions in terms of pollutants degradation [23]. Many reasons might be involved behind this phenomenon. If the Fenton reaction started with Fe²⁺, the release of ‘OH occurs which is the second strongest oxidizing agent (E° = 2.80 V), whereas reaction with Fe³⁺ results in less powerful ‘OH oxidant (E° = 1.65 V). The Fenton’s reaction (eq. (13)) has a higher rate constant (k = 63 M⁻¹s⁻¹) than the Fenton-like reaction (eq. (17)) (k = 0.002–0.01 M⁻¹s⁻¹); the later reaction becomes a rate limiting step and reduces the ‘OH production rate in chemical Fenton systems where Fe²⁺ is not continuously regenerated ‘OH [119].

As shown in Table 2, a wide variety of iron sources either homogeneous [23,24,28,120,121] or heterogeneous [35,122,123] have been

| Table 1: Pros and Cons of various major membranes, summarized from the corresponding references [102-103,114,198-200]. |
|---|---|---|
| Membrane | Pros | Cons |
| CEM/PEM | • Good mechanical strength | • Highly expensive (Nafion) |
| | • High proton transfer rate (Nafion) | • Oxygen and substrate crossovers |
| | • Excellent chemical and electrochemical stabilities | • Transport of cations other than protons |
| | • Lower activation resistance | • Membrane choking and biofouling (Nafion) |
| | • Use of non-noble metal & functionalized carbon catalysts | • More susceptible to deformation |
| | • Extensive selection of cheaper materials | • Membrane degradation in alkaline environment |
| AEM | • Rapid catalysis of cell reactions e.g., ORR | • Brittle |
| | • Lesser activation losses | • Loss of anolyte through evaporation |
| | • Use of non-noble metal & functionalized carbon catalysts | |
| | • Extensive selection of cheaper materials | |
| | • Rapid proton transfer with supplementing phosphate or carbonate buffers, resulting in high voltage output | |
| Ceramic | • Water management, crossover and cathode flooding | |
| | • Low-cost/easy availability | |
| | • Simple to wash | |
| | • High chemical and mechanical strength | |
| Composite | • High proton conductivity | • Oxygen crossover |
| | • Membrane hydrophilicity | • Higher surface roughness causes biofouling (3D membrane) |
| | • Higher porosity | |
| | • Low cost | |
| Graphene-based | • High proton conductivity | • Antibacterial effect |
| | • Excellent mechanical stability | • Complicated and energy inefficient graphene synthesis procedure |
| | • Low internal resistance | • High capital cost for scale up applications |
| | • More capability of water uptake | |

applied in MEF systems. Iron (II) sulfate heptahydrate (FeSO₄·7H₂O) is the reduced iron (Fe⁰) and the trivalent form is the iron oxide (Fe³⁺). Moreover, the iron content is higher in Fe⁰ species (Table 3). These iron catalysts were also used in EF studies either in pure forms [131,132], doped with other cations [133], or mostly as composite electrodes [134,135]. Furthermore, some researchers have used iron alginate beads [53,136], scrap iron [22] or iron plates [33,137] as Fenton catalyst (Table 2).

Recently, the MEF studies proposed the use of self-designed electrodes such as Fe@Fe₂O₃/C [25,27,34,138], γ-FeOOH/CF [31], carbon nanotube (CNT)/γ-FeOOH/CF [15], PPy/AQDS/CF [35] and FeVO₄/CF [139] composite cathode, all of which provide iron catalyst via homogeneous or heterogeneous reactions, as explained in section 4.4. This practice minimizes the iron sludge to a great extent and extends the operating pH range. However, the high cost of fabricating iron-containing electrode also limits its application to some extent. Therefore, more research is needed to discover a new and low cost iron source with high efficiency and long-time stability for the application of MEF system.

5.2. Electrolytes

5.2.1. Anolyte

The anolyte has two important functions: it provides the nutrients for the microorganisms and a conductive medium to support current flow in the electrochemical cell. Neutral or circum neutral electrolytes are generally used which contain inorganic nutrients (NaHCO₃, NH₄Cl, KCl, phosphate buffer (NaH₂PO₄ and Na₂HPO₄)) and a source of carbon (glucose, acetate and lactate) for the microbial communities. The organic matter present in wastewater and agricultural or domestic wastes can also be a source of carbon [24,25]. However, it is pertinent to note that the complex composition of real effluents may have an important impact on the microbial communities due to the presence of refractory and toxic compounds. Consequently, low COD removal and current efficiencies are generally achieved [5,27,50].

The electrolyte pH is an important factor which can critically affect the overall MET/MEF performance. In particular, the pH affects the microbial consortia and their growth conditions, and pH shifts can

<table>
<thead>
<tr>
<th>Fe source</th>
<th>Method of incorporating Fe catalyst</th>
<th>Fe dose</th>
<th>Initial pH</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogeneous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>5 mg Fe²⁺ L⁻¹</td>
<td>2</td>
<td>[30]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>300 mg FeSO₄ L⁻¹</td>
<td>3</td>
<td>[24]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>300 mg FeSO₄ L⁻¹</td>
<td>2</td>
<td>[23]</td>
</tr>
<tr>
<td>FeCl₃·6H₂O</td>
<td>Directly added to catholyte</td>
<td>150-500 mg FeCl₃ L⁻¹</td>
<td>3</td>
<td>[22]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>1.25 mM Fe²⁺</td>
<td>3</td>
<td>[28,121]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>10 mM Fe²⁺</td>
<td>3</td>
<td>[201]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>7.5 mM Fe²⁺</td>
<td>2</td>
<td>[32]</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>Directly added to catholyte</td>
<td>0.5 mM Fe²⁺</td>
<td>2-3</td>
<td>[49]</td>
</tr>
<tr>
<td>Heterogeneous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-FeOOH/CF</td>
<td>γ-FeOOH/CF composite cathode</td>
<td>2000 mg Fe²⁺</td>
<td>7</td>
<td>[31]</td>
</tr>
<tr>
<td>Limonite</td>
<td>Directly added to catholyte</td>
<td>112 mg Fe²⁺</td>
<td>2</td>
<td>[123]</td>
</tr>
<tr>
<td>Fe₂O₃/C</td>
<td>Fe₂O₃/C composite cathode</td>
<td>3</td>
<td>[25,27,34,50,138,202]</td>
<td></td>
</tr>
<tr>
<td>CNT/γ-FeOOH/C</td>
<td>CNT/γ-FeOOH composite cathode</td>
<td>7</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>Clino-pyrrhotite (Fe₁₋ₓS)</td>
<td>Fe₁₋ₓS - coated graphite cathode</td>
<td>5.4</td>
<td>[127]</td>
<td></td>
</tr>
<tr>
<td>FePO₄</td>
<td>FePO₄/CF composite cathode</td>
<td>7</td>
<td>[36]</td>
<td></td>
</tr>
<tr>
<td>PPy/AQDS/CF</td>
<td>PPy/AQDS/CF composite cathode</td>
<td>7</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>FeVO₄</td>
<td>Prepared by wet chemical process and added to catholyte</td>
<td>800 mg FeVO₄</td>
<td>3</td>
<td>[162]</td>
</tr>
<tr>
<td>Fe₂O₃/ACF</td>
<td>Fe₂O₃/ACF composite cathode</td>
<td>2</td>
<td>[163]</td>
<td></td>
</tr>
<tr>
<td>Phthalocyanine (FePc)-based catalyst</td>
<td>FePc/EG/PTFE composite cathode</td>
<td>7</td>
<td>[36]</td>
<td></td>
</tr>
<tr>
<td>FeVO₄/C</td>
<td>FeVO₄/CF composite cathode</td>
<td>7</td>
<td>[139]</td>
<td></td>
</tr>
<tr>
<td>PPy/AQDS/CF</td>
<td>PPy/AQDS/CF composite cathode</td>
<td>7</td>
<td>[35]</td>
<td></td>
</tr>
<tr>
<td>Phthalocyanine (FePc)-based catalyst</td>
<td>FePc/EG/PTFE composite cathode</td>
<td>7</td>
<td>[36]</td>
<td></td>
</tr>
<tr>
<td>Iron objects</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immobilized iron</td>
<td>5/10 g iron beads added to catholyte</td>
<td>150 mg Fe²⁺ L⁻¹</td>
<td>2</td>
<td>[53,136]</td>
</tr>
<tr>
<td>Scrap iron</td>
<td>Added to catholyte</td>
<td>10,000 mg Fe²⁺</td>
<td>3</td>
<td>[22]</td>
</tr>
<tr>
<td>Iron plate</td>
<td>Inserted as anode</td>
<td>3</td>
<td>[33]</td>
<td></td>
</tr>
<tr>
<td>Iron sheet</td>
<td>Inserted as cathode</td>
<td>3</td>
<td>[137]</td>
<td></td>
</tr>
</tbody>
</table>
Table 3  Physico-chemical properties of iron oxides.

<table>
<thead>
<tr>
<th>Iron oxide</th>
<th>Chemical formula</th>
<th>Crystal system</th>
<th>Density (g·cm⁻³)</th>
<th>Colour</th>
<th>Surface area (m²·g⁻¹)</th>
<th>pH content (%)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄ (ideal formula, Fe₃O₄)</td>
<td>Cubic</td>
<td>5.18</td>
<td>Black</td>
<td>2–90</td>
<td>73</td>
<td>Most abundant iron oxide with Fe²⁺ that enhances -OH release via Fenton’s reaction. The occurrence of octahedral sites in its arrangement that are generally at the surface of the crystal and the catalytic activity is mainly due to the octahedral cations. Production of more active sites after modifying its physico-chemical characteristics via isostructural substitution by various transition metals.</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
<td>Trigonal</td>
<td>5.26</td>
<td>Red</td>
<td>100–400</td>
<td>61–70</td>
<td>Hematite is Fe³⁺ containing iron oxide. α-Fe₂O₃ is the most important polymorph existing in nature as hematite. Its nanoparticles can be separated from the reaction mixture by means of an external magnetic field and used again for additional reactions as an ecological point of view.</td>
</tr>
</tbody>
</table>

The anodic organic matter removal efficiency was declined with effluent COD increasing from 549 ± 265 mg COD L⁻¹ d⁻¹ to 883 ± 91 mg COD L⁻¹ d⁻¹. It was due to the acidic pH, which proved to be unfavorable for the anodic microorganisms; secondly, the generated H₂O₂ and -OH in the cathode chamber might have bactericidal effect on the anodic microorganisms. As oppose to non-bio electrochemical systems, a near-neutral pH is essential for the bioanolyte and a decline of anodic pH would lead to a severe loss of microbial activity [143].

5.2.2. Catholyte

With respect to the catholyte, Na₂SO₄ has been the most common choice as can be seen in Table 4. However, some works have reported Cl⁻ ions, PBS at neutral pH and the wastewater itself with high conductivity. HClO₄ and NaNO₃ have also been used with similar or even higher performances, which has been attributed to their inertness with -OH and the lack of complexation with iron ions [144,145]. Nonetheless, these species have only been used for research purposes owing to environmental implications. Regarding Cl⁻ ions, it is known that Cl⁻ is a -OH scavenger that affects the Fenton’s reaction at concentration higher than 0.01 M in acidic medium [146,147]. The oxidation on Cl⁻ ions leads to chloride radicals following eq. (35)–(37); these radicals being less reactive than -OH [146]. On the other hand, it is known that PO₄³⁻ ions form insoluble and less reactive complexes with Fe (pH-dependent) which diminishes the efficiency of the Fenton’s reaction in acidic solutions [148,149]. However, high removal efficiencies have been obtained when using neutral-pH PBS as supporting electrolyte in MEF systems. In general, PBS solutions have been used in heterogeneous systems where the catalyst is either suspended in the solution or coated on the cathode [15,36]. In heterogeneous systems, surface reactions play a crucial role in the formation of the oxidants and thus in the degradation of the pollutants [101]. Hence, a report suggested that the oxidation of the dye Congo red in the cathodic chamber of a MEF system (PBS electrolyte) was achieved by means of high-valent iron-oxo species formed on the surface of the iron-phthalocyanine heterogeneous catalyst rather than via Fenton-derived -OH [36].

\[
\begin{align*}
\text{Cl}^- + \text{-OH} &\rightarrow \text{ClO}^- \text{H}^- \\
\text{ClO}^- + \text{H}^+ &\rightarrow \text{Cl}^- + \text{H}_2\text{O} \\
\text{Cl}^- + \text{Cl}^- &\rightarrow \text{Cl}_2^- 
\end{align*}
\]

(35)  (36)  (37)

In the catholyte of the MEF, the course of reaction between Fe³⁺ ions and H₂O₂ (Fenton’s reaction) depends on the pH, which is mainly related to the speciation of Fe⁴⁺/Fe³⁺ ions in aqueous solution [12,147]. MEF studies suggest that the Fenton’s reaction occurs at an acidic pH between 2 and 4, where the maximum production of -OH is expected from Fenton’s reaction according to eq. (13). At pH higher than 3, iron species precipitate as ferric hydroxides (FeOH)₃ (eq. (38)), and this undesirable reaction leads to a decrease in the performance [150]. Moreover, H₂O₂ is not stable at alkaline medium and rapidly decomposes to oxygen and water (eq. (39)) [151]. On the other hand, at pH lower than 1, the reaction is restricted to the oxidation of Fe²⁺ ions by H₂O₂ (eq. (40)) [152].

\[
\begin{align*}
\text{Fe}^{3+} + 3\text{OH}^- &\rightarrow \text{Fe(OH)}_3 \\
\end{align*}
\]

(38)
Table 4
Summary of MEF studies reported in literature dealing with various wastewaters and target pollutants.

<table>
<thead>
<tr>
<th>WW/target pollutant</th>
<th>Reactor type</th>
<th>Electrode</th>
<th>Membrane</th>
<th>Operating conditions</th>
<th>Pollutant removal</th>
<th>Max. electricity production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real landfill leachate</td>
<td>H-type bottle reactor/DC</td>
<td>CF</td>
<td>CF</td>
<td>CEM (CMI-7000, Membrane Int’l USA)</td>
<td>Total electrolyte working vol.: 360 mL (real effluent with high Cl⁻ content), Operation mode: batch, Electrode distance: 3 cm, Temp.: 25 ± 1°C, Iron source: FeSO₄·7H₂O</td>
<td>49.3 ± 6.5% COD</td>
</tr>
<tr>
<td>Real landfill leachate</td>
<td>Rectangular shaped/DC</td>
<td>GAC + graphite granules embedded between SS wire mesh alternatively</td>
<td>SS wire mesh</td>
<td>CEM (CMI-7000, Membrane Int’l USA)</td>
<td>Total electrolyte working vol.: 1100 mL (real effluent with high Cl⁻ content), Operation mode: continuous, Electrode distance: 3 cm, Temp.: 25 ± 4°C, Iron source: FeSO₄·7H₂O</td>
<td>838 ± 91 mg COD L⁻¹d⁻¹</td>
</tr>
<tr>
<td>Real landfill leachate</td>
<td>SC</td>
<td>–</td>
<td>nZVI@AC</td>
<td>–</td>
<td>Total electrolyte working volume: 28 mL, carbon source: 1 g/L acetate, External resistance: 1000Ω, iron source: nano-zero-valent iron composite, Operation mode: batch.</td>
<td>–</td>
</tr>
<tr>
<td>Medicinal herbs WW</td>
<td>Rectangular shaped/DC</td>
<td>CF</td>
<td>Fe@Fe₂O₃/CF composite cathode</td>
<td>Nafion 112, DuPont Co., USA</td>
<td>Total electrolyte working vol.: 100 mL, Operation mode: batch, Temp.: 30°C, cathodic pH: 3.0 (real effluent with SO₄²⁻ content), Air flow rate: 300 mL min⁻¹</td>
<td>8.05% COD</td>
</tr>
<tr>
<td>Brewery WW</td>
<td>Identical chambered reactor/DC</td>
<td>CF</td>
<td>Fe@Fe₂O₃/NCF composite cathode</td>
<td>GORE-TEX® cloth (Zhejiang, China)</td>
<td>Total electrolyte working vol.: 150 mL, Operation mode: continuous, Catholyte pH: 3.0 (2% NaCl), Air flow rate: 300 mL min⁻¹</td>
<td>–</td>
</tr>
<tr>
<td>Real landfill leachate</td>
<td>DC</td>
<td>CF</td>
<td>Pyrrhotite-coated graphite-cathode</td>
<td>CEM (CMI-7000, Ultrex)</td>
<td>Total electrolyte working vol.: 850 mL, Catholyte pH: 5.4 (1 M KCl), Distance between electrode &amp; PEM: 3 cm</td>
<td>–</td>
</tr>
<tr>
<td>Coal gasification WW</td>
<td>DC</td>
<td>CF</td>
<td>FeVO₄/CF cathode</td>
<td>Nafion 212, DuPont Co., USA</td>
<td>Total electrolyte working vol.: 100 mL (0.1 M Na₂SO₄), Operation mode: batch, Temp.: 30°C, Distance between electrode &amp; PEM: 3 cm, Air flow rate: 100 mL min⁻¹</td>
<td>–</td>
</tr>
<tr>
<td>Swine WW</td>
<td>Coaxial cylindrical reactor/DC</td>
<td>Graphite granules, 868 g</td>
<td>Fe@Fe₂O₃/CF composite cathode</td>
<td>GORE-TEX® cloth (Zhejiang, China)</td>
<td>Total electrolyte working vol.: 800 mL, Operation mode: continuous, Anodic pH: 3.0, Ext. resistance: 100 Ω, Air flow rate: 300 mL min⁻¹</td>
<td>62.3–71.7% BOD₅, 39–46.5% COD, 53.5–58.7% NH₃-N</td>
</tr>
<tr>
<td>Aniline-containing real WW</td>
<td>DC</td>
<td>Carbon fiber brush</td>
<td>Bipolar membrane (IPM, fumasep® FBM, FuMA-Tech GmbH, Germany)</td>
<td>–</td>
<td>Operation mode: batch, Anodic pH: 3.0, Temperature: 20 ± 2°C, Air flow rate: 16 mL min⁻¹, Applied voltage</td>
<td>–</td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>WW/target pollutant</th>
<th>Reactor type</th>
<th>Electrode</th>
<th>Membrane</th>
<th>Operating conditions</th>
<th>Pollutant removal</th>
<th>Max. electricity production</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Industrial dyes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid Orange 7</td>
<td>DC</td>
<td>Iron plate</td>
<td>Carbon paper loaded with 0.05 mg cm$^{-2}$ Pt CF</td>
<td>PEM (GEFC-10N, China)</td>
<td>Total electrolyte volume: 400 mL (0.16 M NaCl), Anode pH of AFT: 3.0</td>
<td>85% AO7</td>
<td>–</td>
</tr>
<tr>
<td>Azo dye (Acid Orange 7)</td>
<td>H-type/DC</td>
<td>CF</td>
<td>Nafion 117 (DuPont Co., USA)</td>
<td>Total electrolyte volume: 160 mL, Operation mode: batch, External resistance: 4 Ω, Temperature: 30°C, Cathodic pH: 2–3 (0.1 M Na$_2$SO$_4$)</td>
<td>–</td>
<td>&gt; 99% color, 70% TOC</td>
<td>0.15–0.49 A m$^{-2}$ [49]</td>
</tr>
<tr>
<td>Azo dye (Orange II)</td>
<td>DC</td>
<td>PPy/AQDS modified CF</td>
<td>CF</td>
<td>PEM (Qianqiu, Zhejiang China)</td>
<td>Total electrolyte volume: 140 mL, Operation mode: batch, External resistance: 1000 Ω, Temperature: 30°C, Cathodic pH: 7.0 (0.1 M PBS), Air flow rate: 100 mL min$^{-1}$</td>
<td>–</td>
<td>$k_{TOC}$: 0.06–0.145 h$^{-1}$</td>
</tr>
<tr>
<td>Orange II</td>
<td>Rectangular shaped DC reactor</td>
<td>CF</td>
<td>CNT/FeOOH composite cathode</td>
<td>PEM (Qianqiu Group Co., Ltd. China)</td>
<td>Total electrolyte volume: 142 mL, Bacterial culture: Shewanella decolorationis S12, Operation mode: batch, External resistance: 1000 Ω, Temperature: 30°C, Cathodic pH: 3</td>
<td>–</td>
<td>Complete decolorization in 14 h, Complete mineralization of Orange II in 43 h</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>Plexiglas-made DC reactor</td>
<td>CF</td>
<td>NFC, NCF/Fe$^{2+}$, NCF/Fe$_2$O$_3$ composite cathode</td>
<td>GORE-TEX® cloth</td>
<td>Total electrolyte volume: 140 mL, Anolyte: Brewery WW, Catholyte: synthetic dye WW containing RhB, External resistance: 1000 Ω, Temperature: 30°C, Cathodic pH: 3</td>
<td>–</td>
<td>79–95% decolorization with Fe$_2$O$_3$/NCF cathode</td>
</tr>
<tr>
<td>Congo Red</td>
<td>MFC-COR setup</td>
<td>Graphite granules with graphite rod</td>
<td>Anthraquinone-based spherical catalyst and graphite rod</td>
<td>PEM, Nafion 117 (DuPont Co., USA)</td>
<td>Total electrolyte volume: 200 mL, Air flow rate: 8 mg L$^{-1}$, External resistance: 1000 Ω, Temperature: 20 ± 3°C, Cathodic pH: 7 (PBS)</td>
<td>–</td>
<td>90% Congo red in 72 h</td>
</tr>
<tr>
<td>Lissamine Green B, Crystal Violet</td>
<td>H-Type bottle reactors</td>
<td>Graphite rod</td>
<td>Graphite rod</td>
<td>Sterion® CEM</td>
<td>Electrolyte volume: 250 mL (0.1 M Na$_2$SO$_4$), Electrode distance: 12 cm, catholyte pH: 2, Air flow rate: 21 mm$^{-1}$, External resistance: 1000 Ω, Temperature: 20 ± 3°C, Cathodic pH: 7 (PBS)</td>
<td>–</td>
<td>70–82% TOC, 94% LG, 83% CV</td>
</tr>
<tr>
<td>Lissamine Green B, Crystal Violet, Indigo Carmine, Reactive Black 5</td>
<td>Hybrid cell (Benthic MFC and EF cell)</td>
<td>Graphite sheets</td>
<td>Graphite sheet</td>
<td>Salt bridge</td>
<td>Anolyte volume: 1000 mL, Catholyte volume: 1500 mL (0.01 M Na$_2$SO$_4$), Air flow rate: 1 L min$^{-1}$, Operation mode: continuous</td>
<td>–</td>
<td>98.2% LG, 96.2% CV, 97.2% IG, 88.2% RB5</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>H-type DC</td>
<td>Carbon fiber brush</td>
<td>Graphite plate/Platinized carbon paper</td>
<td>Bipolar membrane (FUMA-Tec GmbH, Germany)</td>
<td>Total electrolyte volume: 550 mL, catholyte pH: 3 (0.1 M Na$_2$SO$_4$), Electrode distance: 3 cm, External resistance: 5 Ω, Temperature: 25 ± 5°C,</td>
<td>–</td>
<td>0.43 h$^{-1}$ decolorization, 0.22 h$^{-1}$ MB mineralization</td>
</tr>
</tbody>
</table>

**Emerging contaminants**
<table>
<thead>
<tr>
<th>WW/target pollutant</th>
<th>Electrode Membrane Operating conditions</th>
<th>Pollutant removal</th>
<th>Max. electricity production</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol, Bisphenol A, Estrogen, Sulfamethazine, Triclocarban</td>
<td>Anode: CF, Cathode: Graphite granules, Membraneless</td>
<td>Total electrolyte volume: 80 mL, Catholyte pH: 3</td>
<td>81% 17α-estradiol, 56% 17β-estradiol</td>
<td>[33]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 128 mL, Catholyte pH: 3</td>
<td>90–100% E1, 64–72% BPA, 56–99% TCC, 56–100% SM2</td>
<td>[28]</td>
</tr>
<tr>
<td>Phenol, Bisphenol A, Estrogen, Sulfamethazine, Triclocarban</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 150 mL, Catholyte pH: 3</td>
<td>81% 17α-estradiol, 56% 17β-estradiol</td>
<td>[33]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite granules, Membrane: PEM</td>
<td>Total electrolyte volume: 240 mL, Catholyte pH: 3</td>
<td>90–100% E1, 64–72% BPA, 56–99% TCC, 56–100% SM2</td>
<td>[28]</td>
</tr>
<tr>
<td>Phenol, Bisphenol A, Estrogen, Sulfamethazine, Triclocarban</td>
<td>Anode: CF, Cathode: Graphite granules, Membrane: PEM</td>
<td>Total electrolyte volume: 240 mL, Catholyte pH: 3</td>
<td>90–100% E1, 64–72% BPA, 56–99% TCC, 56–100% SM2</td>
<td>[28]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 300 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
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<td>Phenol</td>
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<td>[123]</td>
</tr>
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<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
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<td>[123]</td>
</tr>
<tr>
<td>Phenol</td>
<td>Anode: CF, Cathode: Graphite plate, Membrane: PEM</td>
<td>Total electrolyte volume: 170 mL, Catholyte pH: 2</td>
<td>96% p-nitrophenol</td>
<td>[123]</td>
</tr>
<tr>
<td>WW/target pollutant</td>
<td>Reactor type</td>
<td>Anode</td>
<td>Cathode</td>
<td>Membrane</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------</td>
<td>-------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>Arsenite (As III)</td>
<td>Rectangular DC</td>
<td>CF</td>
<td>GF/γ-FeOOH composite cathode</td>
<td>CEM (Qianqiu, Zhejiang China)</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>SC</td>
<td>Carbon brush</td>
<td>Carbon cloth-based gas diffusion cathode</td>
<td>–</td>
</tr>
<tr>
<td>Triphenyltin chloride</td>
<td>DC</td>
<td>GF</td>
<td>GF/Fe@Fe₂O₃ composite cathode</td>
<td>PEM, Nafion 117 (DuPont Co., USA)</td>
</tr>
</tbody>
</table>

The acidic pH effluents need final neutralization of the treated water before its discharge, resulting in extra cost coupled with iron sludge production. This problem can be avoided using heterogeneous Fenton-like catalysts in MEF systems at neutral pH. The details about these systems have been given in section 5.1.

5.3. Temperatures

Temperature can significantly affect the overall MET/MEF performance, especially in the anode chamber. Literature suggests that MEF system has been mostly conducted at temperature range of 25–35°C. Previous investigations have discovered that electrochemically active microbes can grow well at an operational temperature of 30°C [153,154]. Variations in temperature impart clear influence on system kinetics and mass transfer, MFC thermodynamics, and the nature and diversity of the microbial community [141]. In a single chambered MFC, Ahn and Logan [155] found somewhat high values of CE (47–50%) after changing the temperature from 23 to 30°C. Larrosa-Guerrero [156] tested the effect of temperature ranging from 20 to 35°C using both a single and a two-chambered MFC. The results indicated no significant change in COD removal efficiency with the temperature shifts (dual chamber: 75–82% versus single chamber: 90–95%). The CE was low in all cases (CE 0.7–1.8%). Employing a single chamber air cathode MFC, Michie et al. [157] observed the influence of temperature (10, 20 and 35°C) on the system performance. The highest COD removal rate of 2.98 g COD L⁻¹ d⁻¹ was attained in the reactor controlled at 35°C, however significantly higher CEs were obtained at psychrophilic temperatures. In a recent investigation, Tremouli et al. [140] observed that maximum power density and CE were both improved by 64% and 211%, respectively, when the operating temperature was increased from 24 to 35°C. The COD removal efficiency remained almost constant (75–80%) for all pH and temperature variations. These findings reflect that the METs can be promising for the regions with warm climate since higher temperatures improve its performance.

6. Environmental application of MEF systems

As illustrated in Table 4, MEF systems have environmental application ranging from a wide variety of wastewaters and target pollutants such as a number of industrial dyes and various classes of emerging contaminants.

6.1. Real wastewaters

MEF processes were employed in several investigations to treat a wide variety of real wastewaters containing biorecalcitrant organics. In our previous experiments, real landfill leachate pre-treated with partial nitritation-anammox process was employed in both anode (as substrate) and cathode chambers to remove refractory organic pollutants, simultaneously coupled with electricity production [23,24]. The first work [23] was carried out in a set of H-type bottle reactors with net effective volume of 360 mL, with CF electrodes separated by CEM, (CMI, 7000, Membrane Int’l., USA). In the potentiostatic mode experiment (479 mV vs. SHE), the system attained a simultaneous anodic and cathodic COD removal of 71–76% and 77–81%, respectively, with glucose as anode substrate and the landfill leachate as catholyte. The COD removal and CE were affected when the system was switched to landfill leachate substrate, but the current density throughout the experiment was constant (1.7 A m⁻²). In our second work [24], two different MEF configurations with total working volume of 1100 mL were operated employing landfill leachate as the anolyte and the catholyte. Despite low biodegradable organic content in the landfill leachate (2401 ± 562 mg COD L⁻¹; 237 ± 57 mg BOD₅ L⁻¹), the technology was capable of reaching COD removal rates of 1077–1244 mg L⁻¹ d⁻¹ with simultaneous electricity production of 43.5 ± 2.1 Am⁻³ cathodic displacement volume. The recirculation of acidic catholyte into anode chamber halted the anodic efficiency owing to pH stress on anodic microbes. These results revealed that the integrated system is a potentially applicable method to deal with biorefractory organic matter present in mature landfill leachate. Employing real landfill leachate substrate, Wang and co-researchers, revealed higher COD removal of 72.2–83.8%, CE of 27.8–30.6% and power output of 0.9–1.0 Wm⁻², in a single chambered MEF cell using nano-zero-valent iron doped activated carbon electrode (denoted as nZVI@MAC) [92].

In another investigation, Li and co-team integrated cathodic pyrrhotite-catalyzed Fenton’s reaction with anodic microbial respiration for the improvement of MFC performance and treatment of a real landfill leachate [127]. The MFC furnished with a pyrrhotite-coated graphite-cathode produced the maximum power density of 4.2 W m⁻³ that was 133% higher than simple graphite-cathode. Concurrently, the polarization resistance of pyrrhotite-cathode (92 Ω) was much lower than the graphite-cathode (1057 Ω), evidencing that the cathode overpotential was considerably lowered, perhaps because of the pyrrhotite Fenton’s reaction. Moreover, the system removed 77% of color and 78% of COD from the real landfill leachate, demonstrating that the pyrrhotite not only represented a cheaper catalyst for MFCs in power output, but also catalyzed the degradation biorecalcitrant compounds.

Noushin Birjandi et al. [25] applied the MEF process to treat the medicinal herbs wastewater in a dual-chamber MFC with Nafion membrane as a separator. Under optimal conditions, the MEF system equipped with a Fe@Fe₂O₃/graphite composite cathode (0.9 g FeCl₃·6H₂O), and Nafion 112 showed the highest OCV (600 mV), power density (60.43 mW m⁻²), CE (4.09%) and energy conversion efficiency (1.37%) among the other MEF systems examined. Moreover, the system removed 78% and 84% of COD from anode and cathode, respectively. To deal with the swine wastewater, a cylindrical MEF system with an effective inner cathodic and outer anodic volume of 350 and 450 mL, respectively was employed, separated by Gore-Tex cloth [27]. The system efficiency was analyzed at two different organic loading rates (OLR) of 1.1 g COD L⁻¹ d⁻¹ and 4.6 g COD L⁻¹ d⁻¹. As shown in Table 4, at both OLRs, the overall removal rate of BOD₅, COD, NH₃-N and TOC was in the range of 62–95%. Moreover, the Fe@Fe₂O₃/CF composite electrode-laden system attained a maximum power output ranging from 3 to 8 W m⁻³, with 60–65% CE. More recently, an experiment was carried out aiming at testing the feasibility of the MEF system with a new composite cathode (FeVO₄/CF) to treat coal gasification wastewater [139]. The system achieved a maximum power density of 849.7 mW m⁻³, along with 92.3% of COD, 91.5% of TOC and 85.7% of total phenols removal in the cathodic chamber. Moreover, the authors claimed that FeVO₄/CF could be used as a two-way Fenton-like catalyst that can produce more reactive oxygen species.

Aniline (C₆H₅NH₂) containing wastewater can cause major environmental difficulties and threat humans’ health. Yet, rapid elimination of aniline with cost-effective techniques remains a challenge. Recently, Li and co-researchers claimed a novel combination of MEC-based Fenton system with bipolar membrane to deal with real wastewater with a high concentration of aniline (4460 ± 52 mg L⁻¹) [26]. The aniline was degraded following first-order kinetics at a rate constant of 0.0166 h⁻¹ under an applied potential of 0.5 V. Similarly, a TOC abatement efficiency of 93.1 ± 1.2% was found, revealing efficient mineralization of aniline.
6.2. Recalcitrant pollutants

6.2.1. Industrial dyes

Industrialization plays a key role in economic growth and social uplift of any country. However, it is also directly linked with environmental deterioration, ecosystem disturbances and human health problems. The Blacksmith Institute and Green Cross, Switzerland [158] reported that around 125 million inhabitants living in 49 low- to middle-income countries are at risk of industrial pollution. For instance, the total environmental load in Phnom Penh city, Cambodia (a highly populated country) was estimated to be 476,981 Mg including 189,109 Mg VOC, 165,411 Mg of toxic chemicals in air, 38,523 Mg of toxic chemicals in land and 28,968 Mg of SO2 in 2014. Textiles and Apparel sector contributed with the highest production of toxic chemicals (434,016 Mg of total pollution) load to air, aquatic and terrestrial environments [159]. Blacksmith Institute found that the public health impact, measured in disability adjusted life year (DALY), is almost the same or higher for industrial pollutants (17,147,600) than some of the most dangerous diseases such as tuberculosis (25,041,000), HIV/AIDS (28,933,000) and malaria (14,252,000) worldwide [158].

With the expansion of the various industries, dye accounts for a very huge fraction of wastewater in the organic pollution. Azo dyes, characterized by the chromophore group (−N=N−) has been highly adopted in dyeing industry [160]. Owing to non-degradability, potential mutagenicity and poor biochemical purification ability, azo dyes are not only a direct threat to people's health, but also pose a major risk to the soil environment but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects”.

Recently MEF processes have been employed to deal with various emerging contaminants or contaminants of emerging concerns (CECs) is long; however the most significant classes of CECs are illustrated in Fig. 5. The United States Geological Survey gives a significant definition of CECs: “any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects”.

Discharge of CECs into the environment has raised great concerns owing to their adverse impacts on the ecosystem. Traditional wastewater treatment plants (WWTPs) with biological treatment processes are reported to abate varying degrees of CEC from wastewater [164-166]. Nonetheless, the remaining CEC and their transformation products in the WWTPs effluents are still a grave issue for the receiving environment and downstream inhabitants [167].

Recently MEF processes have been employed to deal with various classes of CECs such as pharmaceuticals, antibiotics, endocrine disrupting chemicals (EDCs), pesticides, personal care products (PCPs) etc. (Table 4). Wang et al., examined the application of MEF system for the abatement of four CECs including Bisphenol A (BPA), Estrone (E1), Sulfamethazine (SM2) and Triclocarban (TCC). The glucose-fed MEF system generated the maximum H2O2 concentration (0.36–2.06 mg L−1) compared to the acetate-fed configuration (0.08 mg L−1). This probably could be attributed to the widespread microbial consortia in glucose-fed MEF system due to the production of diverse glucose fermentation byproducts such as acetate and butyrate.
leading to the rapid current production [168]. Hence, higher power output was achieved in glucose-fed MEF (0.29–1.11 W m−3) than acetate-laden system (0.22 W m−3) in the aforementioned study. In batch mode, the removal efficiencies for E1, BPA, TTC and SM2 were 90–100%, 65–73%, 58–99% and 56–100%, respectively, within 24 h, whereas in continuous mode the corresponding removals were 94–100%, 64–75%, 62–98%, and 62–97%. The elimination was attributed to the adsorption onto the graphite electrodes and the oxidation by ‘OH from Fenton reaction.

As an emerging contaminant, the strobilurin fungicide pyraclostrobin (methyl 2-[1-(4-chlorophenyl) pyrazol-3-yloxymethyl]-N-methoxy carbamate) has been often spotted in aquatic environments, including surface water and groundwater. Moreover, this pollutant has a potential threat to humans [169]. In a recent study [121], the degradation of pyraclostrobin was carried out by microbial degradation and EF oxidation. After 12 h, the removal rate of pyraclostrobin in the anode and cathode chamber was 1.4 mg L−1 h−1 and 1.7 mg L−1 h−1, respectively. The pyraclostrobin concentration was reduced below the detection limit (0.1 mg L−1) at the anodic (72 h) and cathodic chambers (24 h). A maximum of 1.2 mg L−1 of H2O2 was reached after 20 h reaction during the EF process.

The widespread extent of EDCs in wastewaters and their adverse effects on human and animal health has become a serious environmental concern and attracted extensive research. EDCs consist of a wide variety of chemicals, among them steroid hormones including natural estrogen 17β-estradiol (E2) and synthetic estrogen 17α-ethyl estradiol (EE2) are considered as the most dangerous [170–172]. The feasibility of abating estrogens including E2 and EE2 was studied in a MEF system equipped with a Fe@Fe2O3/NCF composite cathode [138]. E2 and EE2 were degraded by reactive oxidants generated by EF process and zero-valent iron/O2 system, as well as by adsorption. The system removed 81% of E2 and 56% of EE2 within 10 h, during which the highest concentration of total iron ions and H2O2 attained 81 and 1.2 mg L−1, respectively. Moreover, the system achieved a maximum power output of 4.35 W m−3.

In a study, Zhu and Ni [22] employed MEF system with scrap iron to eliminate p-nitrophenol (which is an intermediate in the production of paracetamol and also a pH indicator) in wastewater, generating a maximum power output of 143 mW m−2. They achieved complete mineralization of p-nitrophenol within 12 h and TOC removal efficiency of 85% after 96 h duration. Similarly, in another work Tao and co-workers treated the p-nitrophenol wastewater using natural limonite as the iron catalyst in a MET-Fenton system [123]. Under the optimal conditions such as initial p-nitrophenol concentration of 0.25 mM, pH 2.0, external resistance of 20 Ω and limonite dosage of 112 mg, the p-nitrophenol degradation yield was > 96% within 6 h in the MET-Fenton system. In a different study, Zhu and co-workers [33] developed a dual systems using a single chambered MEF as a power source to accomplish the Fenton’s reaction. The system completely mineralized phenol into simple and readily biodegradable organics, along with TOC removal of 75 ± 2% at optimum pH 3 in 22 h. The system produced a maximum power density of 1740 ± 100 mW m−2 (pH 3). Wang et al. [31] studied the oxidation of Arsenite (As III), a well-known carcinogen, in a dual chambered MEF under neutral pH using a CF/γ-FeOOH composite electrode. As (III) depletion followed a first-order rate constant of 0.208 h−1, corresponding to an oxidation current efficiency of 73.1%. The system also attained a maximum power output of 135.3 mW m−2 at a current density of 0.563 A m−2.

Pharmaceuticals and personal care products (PPCPs) are environmental pollutants which pose adverse potential impacts on aquatic species [173,174] and terrestrial media [175]. The group of non-steroidal anti-inflammatory drugs (NSAIDs) such as diclofenac, ibuprofen, ketoprofen and naproxen are known to be used as anti-inflammatory and pain killers. Among them, several are resistant to degradation in conventional wastewater treatment systems, and represent a major environmental and health concern worldwide. Hence it is clear that tertiary treatment of municipal, industrial and hospital wastewater is needed. In a recent study of Nadais and co-workers [52] established a lab-scale MEC-based MEF system for the treatment of four different NSAIDs. At reaction time of 5 h, 59–61% of Ketoprofen, 87–97% of Diclofenac, 80–86% of Ibuprofen and 75–81% of Naproxen were eliminated. However, long reaction times resulted in significant increase in elimination efficiencies for Ketoprofen and Naproxen. Moreover, other optimum parameter values were found to be pH = 2, Fe2+ = 7.5 mM, air-flow = 8 mL min−1, applied potential = 0.3 V. Lastly, results achieved with real wastewater exhibited lower removal rate constants than with distilled water matrices suggesting interferences from wastewater components in the NSAIDs oxidation process. In another study of Zhang and co-workers, paracetamol was eliminated in cathode using a domestic wastewater-laden MEF reactor [30]. A highest 70% paracetamol degradation occurred in 9 h, at optimum conditions i.e. total iron concentration of 5 mg L−1, initial pH of 2.0 and external resistance of 20 Ω. A major portion of paracetamol was mainly transformed to certain intermediates such as p-nitrophenol via p-aminophenol and to less hazardous carboxylic acids. Moreover, the MEF process attained an average power output of 217 ± 23 mW m−2 at a current density of 757 ± 65 mA m−2. Most recently, Wang et al. [32] degraded 90% carbamazepine, a PPCP, in an undivided microbial-electro-Fenton cell with concomitant maximum power density of 112 ± 11 mW m−2, using acetylene black as catalyst for electro-generation of H2O2 and Fe–Mn binary oxide for ‘OH production.

Triphenyltin chloride (TPTC), considered as one of the most extensively used organotin derivatives, has instigated grim environmental impact owing to its high affinity for particulate matter and the trend to enrich in the sediments [176]. Hence, the remediation of soil and water polluted by TPTC is a crucial environmental issue that needs to be addressed. In this regard, MEF system was applied to effective TPTC degradation by Yong et al. [177] inoculating the anode chamber with S. oneidensis MR-1. The system attained a maximum power density of 57.25 mW m−2, with S. oneidensis MR-1 as the exoelectrogen, sodium lactate as the electron donor, O2 as the electron acceptor and a Fe@Fe2O3/graphite felt composite cathode. Moreover, the TPTC elimination efficiency in closed circuit MEF was 78.32 ± 2.07% in 101 h, having degradation rate of 0.775 ± 0.021 μ mol L−1 h−1.

Fig. 5. Classes of ‘contaminants of emerging concerns’ (CECs). PAHs: Polyaromatic hydrocarbons, PCPs: Personal care products.
The EF-treated solution could be further submitted to aerobic treatment and further increased to 0.7 following 120 min treatment. At this point, the outstanding biodegradability of the effluent, EF can be applied as pre- or post-treatment as illustrated in Fig. 6. The fundamentals of this process were recently reviewed in a book chapter [178].

In this scenario, it has been demonstrated that the AOPs, which are based on the generation of powerful •OH (including the electrochemical methods like EF), are capable of breaking down a great variety of complex organic compounds that are in nature refractory to micro-biological attack and thus resistant to conventional biological treatment into simple low-molecular weight species such as short-chain carboxylic acids. Thereby, the biodegradability of the effluents is increased, and treatment can be carried out by conventional microbial-based ways [179, 180]. In this context, it was reported that the biodegradability of refractory solutions of the antibiotic metronidazole in terms of the BOD5/COD ratio (initial BOD5/COD of 0.01) was increased during EF treatment under optimal conditions (0.1 mM of Fe2+ and 0.07 mA cm−2 of current density using an undivided cell equipped with a carbon felt cathode and a Pt anode). The biodegradability threshold from which an effluent is considered to be suitable for biological degradation (BOD5/COD ratio of 0.4) was attained after 60 min of treatment and further increased to 0.7 following 120 min treatment. At 60 min and 120 min of EF treatment, the total organic carbon was still above 70% of the initial content, whereby the authors suggested that the EF-treated solution could be further submitted to aerobic degradation in order to treat the remaining organic content [181].

In another study, Olvera-Vargas et al. [182] showed that short-chain carboxylic acids such as malonic, maleic, oxalic, oxamic, acetic and formic were the main degradation by-products produced after the cleavage of the beta-blocker metoprolol and its aromatic/cyclic intermediates during EF oxidation. These species were responsible for the increase of the solution’s biodegradability during treatment, reaching a BOD5/COD ratio of 0.44 in 60 min time. The 1 h-EF pretreated solution was submitted to aerobic biological degradation using a mixture of pure cultures of microorganisms, which were capable of degrading 81% of the remaining TOC after EF following 4 days of incubation. Overall, 90% of TOC removal was achieved by the sequential Bio-EF process in 1 h of EF and 4 days of aerobic biodegradation, demonstrating EF’s ability to produce biocompatible effluents suitable for biological treatment [183]. The same group highlighted the advantages of the coupled system from an economic and technical perspective since short EF treatment times represent important energetic savings, mainly because it is known that although EF and related electrochemical technologies can achieve high mineralization yields, it requires long energy-consuming treatment times due to the lower reactivity of the degradation intermediates with •OH. Furthermore, treatment time has a direct impact on the electrodes lifespan [182].

It seems that the integration of EF in multi-stage treatment systems is a promising alternative for the treatment of complex industrial effluents taken into consideration that: different pollutants need different treatment approaches, and none wastewater treatment technology is universal. In this regard, some investigations have proposed multi-stage systems incorporating EF and biological methods to treat real industrial wastewaters, such as municipal landfill leachate [184], winery wastewater [185], pharmaceutical wastewater [186, 187] and slaughterhouse wastewater [188].

8. Conclusions, challenges and future perspectives

So far this technology has been successfully applied to deal with some real wastewaters and wide variety of target pollutants such as industrial dye decolorisation and a various classes of emerging contaminants (pharmaceuticals, antibiotics, personal care products, pheno-lic compounds, endocrine disruptors etc.). We believe that this in-depth review will aid as a reference guide for environmental scientists working on MET and MEF systems, and the contextual facts will give assistance in driving further advances on viable solutions for environmental remediation.

Despite the outstanding performance of MEF systems, there are still
some limitations and challenges ahead which need to be addressed to make this promising technology a cost-effective option paving towards scaled-up systems with the aim of meeting the increasingly strict wastewater discharge criteria. The main drawbacks of current MEF systems are: 1) the price of membrane materials, 2) low mineralization efficiencies (COD and TOC removal), 3) low production of current density, 4) several pH adjustment steps in the cathodic compartment, 5) high concentrations of Fe catalyst which entail the generation of secondary sludge, 6) limited research on real wastewaters and 7) lack of efficient reactor designs for scalable systems.

Cathode materials for \( \text{H}_2\text{O}_2 \) production. The use of nanomaterials, such as carbon nanotubes, mesoporous carbon and graphene is a trending area in \( \text{H}_2\text{O}_2 \) electrochemical production for EF applications [86,190]. In this regard, materials scientists working on this field must keep a close collaboration to develop and apply novel materials for all kind of EF processes, including MEF systems. This research also involves composite electrodes containing other sorts of catalysts like layered double hydroxides with alternative transition metals such as Co, Zn, Mg, etc. [133], as well as novel designs of the highly efficient gas diffusion electrodes [87].

Regarding the enhancement of bioelectricity production, the use of the above-mentioned carbon-based nanomaterials with enhanced surface area and electronic properties as anodes could also improve bacterial adhesion, as well as the electron transfer from the microbial communities to the electrode. Nonetheless, the biocompatibility of these kinds of nanomaterials needs to be evaluated in terms of their toxicological and environmental impacts. Additionally, anode modification with alternative polymeric sources and/or redox mediators is a research field under constant development. Here the goal is to develop highly efficient materials to increase the bioenergy outputs that are durable and cost-effective. Three dimensional (3D) electrodes seem to be a potential option. The flat two-dimensional (2D) porous anodes have small pore sizes, which limit the microbial attachment to the inner surface. 3D anodes can overcome this issue by providing larger bioaccessible surface area, which may improve biofilm formation [191]. The same principle is applicable to cathode materials, in which 3D structures provide more electrocatalytic sites for the 2-electron reduction pathway to form \( \text{H}_2\text{O}_2 \).

The acidic pH is another downside of MEF systems. Heterogeneous systems based on Fe-loaded composite electrodes have been applied as an alternative to extend the working pH range of EF systems [192]. Nonetheless, such cathodes involve complex and expensive fabrication methods as well as stability issues; therefore, further research is needed. In addition, other options could be explored following what has been done in heterogeneous EF systems [100]. It includes the use of natural and inexpensive minerals as catalysts (e.g. chalcocpyrite, pyrite, and hematite) [193] and iron-chelating agents such as polyphosphate derivatives [194].

Iron sludge production in the cathode chamber is another problem, which increases the treatment cost. Therefore, more attention should be paid on the electro-regeneration of \( \text{Fe}^{2+} \), which minimizes the production of iron sludge in Fenton oxidation processes. It is noteworthy that quite high amounts of \( \text{Fe}^{2+} \) doses have been used in MEF systems (100–300 mg \( \text{L}^{-1} \)), unlike the small amounts utilized in conventional EF (5.6–27.9 mg \( \text{L}^{-1} \)). Moreover, instead of using conventional homogeneous EF, applying heterogeneous Fenton catalysts in MEF can not only reduce the iron secondary pollution, but also broaden the pH of operation to neutral conditions [100]. This point requires further investigation.

Although some researchers have applied this technology to deal with real wastewaters, there is still need for further research on real effluents under realistic conditions in order to make this technology reliable. The use of real wastewater sources is crucial for determining the main parameters and mechanisms that influence the efficiency of the process since the effects of the matrix are not taken into consideration when working with synthetic wastewaters. Moreover, further investigation of the degradation pathways of organic and inorganic pollutants in MEF systems is required for a better understanding of the chemistry of the process. Future research should include both the anodic and cathodic mechanisms to elucidate the different degradation stages taking place along the treatment.

So far, most of the work on MEF has been conducted at bench scale using small-capacity reactors. The design of MEF systems of higher capacity is compulsory for large scale applications. Novel MEF reactors should incorporate efficient engineering designs aiming at realistic plant operations, especially under continuous flow. The advances in MFC at greater scale [195,196] could be the basis for the conceptualization of pilot MEF systems, in addition to the progress in EF reactors at pilot scale [197]. When considering EF systems, we have to keep in mind that EF reactors generally consist of undivided cells. The challenge is then to adapt/integrate these designs into undivided MEF reactors. Finally, research on modeling of bioelectrochemical systems is highly encouraged as a useful tool for reactor design.

As a final consideration, coupling MEF systems with other bio-, physico-, or chemical- technologies can be considered for the degradation of biorecalcitrant compounds and real wastewater treatment to meet the increasingly strict wastewater discharge criteria.

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References

M. Hassan, et al.


[64] P.V. Sindhesh, H. Holera-Vargas, N. Oturan, M.A. Oturan, Heterogeneous electro-


