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Review

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Bio-Electro-Fenton processes for wastewater treatment: advances and prospects

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Abstract

Water quality deterioration caused by a wide variety of persistent organic pollutants (POPs) has become a serious concern worldwide. Traditional advanced oxidation process (e.g., Fenton reaction) is often inadequate, unsafe, and require post-treatment to remove residual H_2O_2 . In this context, the bioelectrochemical technology assisted advanced oxidation reactions (namely bio-electro-Fenton system) have found a niche where they can become dominant in the near future, especially for POPs removal. Compared to traditional Electro-Fenton technologies, the bio-Electro-Fenton system greatly reduced the expenses on wastewater treatment in terms of electric energy consumption and operation costs. The bio-electro-Fenton system is becoming a versatile platform technology and offers a new solution for emerging environmental issues related to wastewater treatment. This paper critically reviews the existing literature about the degradation of POPs in bio-electro-Fenton system, especially with respect to the treatment performance associated with reactor design and main operating parameters. The review aims to assist researchers and engineers to gain fundamental understandings and critical view of bio-electro-Fenton system, and hopefully with the knowledge it could bring new opportunities for the future development of this promising wastewater treatment technology.

Keywords: Bio-Electro-Fenton systems; Bioelectrochemical technology; Persistent organic pollutants (POPs); Wastewater treatment; Hydrogen peroxide

1. Introduction

Environmental conservation is gradually becoming a matter of major social concern. Biological treatment technologies are the most widespread methods for the organic pollutants treatment, but most of the processes are time-consuming, need large areas, and are ineffective for the degradation of non-biodegradable and toxic pollutants [1]. Fenton process as one of typical advanced oxidation processes is an effective method to completely oxidize persistent organic pollutants (POPs) in wastewater by highly oxidative hydroxyl radicals ($\cdot\text{OH}$) formed from the reaction of H_2O_2 with Fe^{2+} . However, traditional Fenton processes are still costly, energy-intensive and need additional unstable reagents [2-4]. Therefore, low cost and high efficiency Fenton system is required to meet the requirements of pollution control.

Recently, bioelectrochemical systems such as microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and microbial reverse-electrodialysis cells (MRECs), are being developed for diverse applications, especially for wastewater treatment [5, 6]. The biodegradable organic waste could be easily degraded through bacterial oxidation in anode chamber. However, some POPs could not be degraded by the bacterial oxidation in anode chamber. The first MFC-Electro-Fenton system for POPs degradation in cathode chamber was reported by Zhu and Ni in 2009 [7]. Thereafter, the process was named as bio-electro-Fenton and has received increasing attention in recent years resulting in the fast development of a series of bio-electro-Fenton systems [7-12]. One of the typical systems is the MFC based bio-electro-Fenton that anodic electrogenic microorganisms generated electrical power from biodegradable organics to drive the Fenton process occurring in the cathode chamber for oxidation of POPs in wastewater [13]. The most important advantages of bio-electro-Fenton technologies are high efficiency, low toxicity, mild operating conditions, clean treatment

without sludge generation and energy saving. Moreover, the bio-electro-Fenton technologies could be powered by renewable energy from wastewater. The feasibility of bio-electro-Fenton technology has been demonstrated with a wide variety of synthetic wastewater types containing a diversity of target compounds, *e.g.*, azo dyes [10, 11, 14, 15], industrial pollutants [16, 17], and pharmaceuticals [18, 19]. In addition, the processes have been widely studied with respect to pollutants type, pH, wastewater conductivity, electrode material, reactor design, electrode arrangement method, cathode potential and current density distribution [12, 13, 15]. A few excellent reviews have provided information on the MFC-electro-Fenton systems which is one of bio-electro-Fenton systems [13, 15, 20, 21]. However, in recent three years (from 2015), the bio-electro-Fenton systems obtained more attention and advances. More and more new bio-electro-Fenton systems with better performance and new applications were recently reported, such as MEC-Electro-Fenton system, bipolar membrane MEC-Electro-Fenton system, MFC powered MEC-Electro-Fenton system, MREC-Electro-Fenton system and hybrid system of bio-electro-Fenton and traditional wastewater treatment technologies (Fig. 1). Thus, to provide timely update in this important area, this review completely summarizes and systematizes the recently achieved advance, which could pave the way for the further development of the bio-electro-Fenton technology.

Fig.1. is here

In this review, bio-electro-Fenton technologies for the treatment of wastewater contaminated by POPs were discussed in detail with the following goals: (1) to present the fundamental aspects and discuss the impact of the operational parameters and reactor type on their performance; (2) to critically evaluate the advantages and disadvantages of different systems and applications; (3)

forecast the prospect of their utilization in a commercial scale by identifying the key points to be further investigated.

2. Mechanism of bio-electron-Fenton systems

In recent years, bioelectrochemical systems such as MFCs and MECs have been demonstrated as alternative methods for H_2O_2 production. In principle, MFCs consist of bio-anode and cathode compartments by a separator membrane. Organic matters in wastewater are oxidized by the microorganisms growing on the anode, with simultaneous generate electrons and protons. Protons and electrons enter the cathode chamber through the membrane and the external circuit as shown Fig. 2A, then they could react with O_2 to form H_2O_2 in the cathode chamber with simultaneous electricity production. MECs, which are developed from MFCs, require a small amount of electricity input (0.2-0.8V) to generate H_2O_2 in the cathode (Fig. 2B). However, the production rate of H_2O_2 in MECs was much higher than that of MFCs. Compared to conventional electrochemical process, the H_2O_2 production in MECs requires much low energy, which was only 0.93 kWh/kg- H_2O_2 in the reported study [8]. In different bioelectrochemical systems, the optimal H_2O_2 production conditions and maximum H_2O_2 concentration are obviously different (Table 1). For example, the maximum H_2O_2 concentration in MFCs was ranging from 79 to 196 mg L^{-1} with different cathode material and optimized operating parameters [22-25]. Comparatively, the maximum concentration could reach to 1300-1447mg L^{-1} in MECs, which were higher than that of MFCs [8, 26]. The cathode potential as one key parameter for H_2O_2 production on cathode also is varied in different bioelectrochemical systems with different cathode material. For example, Sim et al. found that the maximum H_2O_2 concentration can be obtained at cathode potential of -0.4 V with

graphite as cathode [27]. However, the maximum H_2O_2 concentration of 711.2 mg L^{-1} was observed under the cathode potential of -0.85 V with 0.5 V applied voltage in MEC with three-dimensional electrodes (graphite particle electrodes) as cathode [28]. The cathode material has an important impact on the H_2O_2 production, which requires good electrical conductivity and resistant to corrosion in wide range of pH. The graphene oxide, graphite and carbon cloth have been used in bioelectrochemical system for H_2O_2 production as shown in Table 1. Furthermore, the H_2O_2 generation through oxygen reduction on the cathode surface was affected by the overpotential of electrode. However, most of studies focus on the technical development and improvement of efficiency, none of literature reported the information of the cathode overpotential for H_2O_2 generation in bioelectrochemical systems. To further improve the system performance and determine the mechanisms of catalysis, the cathodic overpotential or cathodic polarization curves for oxygen reduction to H_2O_2 needs to be studied in future work.

Fig.2. is here.

H_2O_2 production has greatly expanded the application possibilities of bioelectrochemical systems. One of the most attractive applications is combining with Fenton reaction for wastewater treatment. The combining systems were named bio-electro-Fenton systems. In general, the bio-electro-Fenton systems consist of two chambers separated by a membrane (e.g., proton-exchange membrane or cation-exchange membrane or bipolar membrane), the mechanism of bio-electro-Fenton systems as shown in Fig. 3. The anaerobic anode is filled with wastewater containing biodegradable organic matters, while the aerobic cathode chamber is filled with wastewater containing POPs. Nearly all bio-electro-Fenton systems share one common principle in the anode chamber, in which biodegradable organic matters are oxidized by microorganisms. The electrons are released from the

oxidation processes at the anode (Eq. 1) and transported to the cathode through an external circuit. The principle is similar with classical bioelectrochemical systems, nearly all the anode materials and microorganisms used in bioelectrochemical systems could also be used in bio-electro-Fenton systems. The electro-Fenton processes mainly occur in cathode chamber. The reaction mechanism of the electro-Fenton process has been elucidated widely. The two-electron reduction of oxygen on the cathode results in H_2O_2 formation (Eq. 2) and then reacts with Fe^{2+} to produce $\cdot OH$ (Eq. 3) for pollutants oxidation [29]. In order to obtain high degradation performance of pollutants in bio-electro-Fenton systems, high H_2O_2 production rate and concentration are necessary. Furthermore, the Fe^{2+} also can be regenerated from the Eq. (4). The reaction mechanism in cathode chamber is similar with the classical Electro-Fenton process.

Table 1. is here.

Fig. 3. is here.

3. Configurations of bio-electro-Fenton systems

Intensive studies in bio-electro-Fenton systems have brought the rapid development in design of new platforms. At present, there have been a wide variety of bio-electro-Fenton systems proposed with different configurations. Based on the different configurations of reactors, bio-electro-Fenton

systems were broadly classified into MFC-Electro-Fenton system, MEC-Electro-Fenton system, MFC powered MEC-Electro-Fenton system, MREC-Electro-Fenton system and MFC powered Electro-Fenton system. Each type of bio-electro-Fenton systems with specific names as shown in Fig. 4, they are discussed in the following sections.

Fig. 4 is here

3.1. MFC-Electro-Fenton system

The MFC-Electro-Fenton system has proven capability to degrade and mineralize POPs in aqueous solution. Zhu and Ni [7] demonstrated for the first time that MFC-Electro-Fenton system not only can remove biodegradable organics in anode chamber, but also can remove POPs in cathode chamber through Fenton-like reaction (see Fig. 4A). Feng et al. [29] also reported the complete decolorization and mineralization of Orange II by MFC-Electro-Fenton system equipped with carbon nanotube (CNT)/-FeOOH composite cathode. The MFC-Electro-Fenton process has several advantages over traditional Electro-Fenton and Fenton processes: (1) no requirement of an external power supply for the electron-Fenton reaction. The electrons are derived from exoelectrogenic bacteria in the anode, and thus, the current is spontaneously produced; (2) better utilization of H_2O_2 and Fe^{2+} than any dosing methods, as both the Fenton reagents can be in situ generated and rapidly used for producing $\cdot\text{OH}$ [15, 29]. However, there are still several limiting factors before its commercial application in wastewater treatment. First, the efficiency of POPs degradation in the MFC-Electro-Fenton system is limited by the pollutants concentration: increasing in initial POPs concentration leads to low degradation efficiency and prolong the time for POPs degradation. One possible reason is that the high concentration POPs may compete with

oxygen for the electron acceptance in the cathode chamber, such as some dyes have been demonstrated as electron accepters [8, 11, 14]. Secondly, low current density and high organic contents may lead to high current efficiency with less energy consumption but require longer times for attaining acceptable mineralization efficiency [11, 22]. Moreover, the H_2O_2 production of MFC is limited, which are insufficient to treat high concentrations of POPs. High mineralization efficiency of the pollutants through the MFC-Electro-Fenton system has only been reported at low pollutant concentration. For instance, Zhuang et al. reported a maximum mineralization efficiency of 90% for 15 mg L^{-1} of rhodamine B dye wastewater in MFC-Electro-Fenton system [40]. Fernandez et al. found the maximum mineralization efficiency of 82% and 70% for 10 mg L^{-1} of Lissamine Green B and 10 mg L^{-1} of crystal violet dye, respectively [41]. Furthermore, most of MFC-Electro-Fenton studies only focus on batch operation. However, from an engineering point of view, continuous feeding of the wastewater in anode and cathode is important. Taking together, it can be concluded that the MFC-Electro-Fenton system is an efficient method for low concentration of POPs. Further development for improving the treatment capacity is still required, for example: (i) modification of anode and cathode for improving the current density and increasing the H_2O_2 production rate; (ii) design low costs of construction with high power output and operate in continuous mode.

3.2. MEC-Electro-Fenton system

MECs have been demonstrated as a promising alternative method for H_2O_2 production [8, 30, 32]. Although MECs require a small amount of electricity supply (0.2-0.8 V), the H_2O_2 production rate and yield are several magnitudes higher than that of MFCs (Table 1). Therefore, MECs could be

more suitable than MFCs for Fenton process in view of H_2O_2 generation capacity. Thus, MEC-Electro-Fenton reactor could be applied for wastewaters containing relatively high concentration pollutants. Compared to the classical Electro-Fenton system, the main difference is using of electroactive bacteria in the anode of MEC-Electro-Fenton system (Fig. 4B). Due to the biological oxidation process of the wastewater organics by the electrogenic microorganisms on the anode could also provide energy, the electrical energy consumption is significantly lower than that of classical Electro-Fenton process, e.g., the MEC-Electro-Fenton process degrade aniline only need 0.5 V external voltage. The electrical energy consumption of $0.728 \text{ kWh kg}^{-1}$ -aniline was hundreds time lower than that of Electro-Fenton process treating aniline with a cost of 74 kWh kg^{-1} -aniline. However, the disadvantage of MEC-Electro-Fenton system is lower POPs removal rate compared to Electro-Fenton system, e.g., the removal rate of aniline in Electro-Fenton system could reach $315 \text{ mg L}^{-1} \text{ h}^{-1}$, while it was only $30.1 \pm 0.4 \text{ mg L}^{-1} \text{ h}^{-1}$ in MEC-Electro-Fenton system [12]. Compared with MFC-Electro-Fenton systems, the MEC-Electro-Fenton system could be used to treat wastewater contained with relative high concentration POPs. The current was enhanced by the application of external power supply, and thus, the removal rates were significantly higher than that of MFC-Electro-Fenton systems. However, due to MEC-Electro-Fenton systems still require external power supply to drive the Fenton process, only few studies focused on this system. The development aimed at increasing system performance (e.g., increasing the current by lowering MEC internal resistance and design rational architecture of MEC) should be pursued. Furthermore, linking MECs with renewable energy sources offers a connection between electricity generation and transportation, stationary and portable energy needs [42]. The electricity generated from wind and solar energy is fully utilized only during high load periods, and is wasted in low load periods. The

excess electricity could be used as power source of MEC-Electro-Fenton system. In this case, the excess electric energy can be used to treat wastewater. Nevertheless, all these hypothesis need to be studied in future work.

3.3. MFC powered MEC-Electro-Fenton system

In order to save the electric energy required on the MEC-Electro-Fenton system, MFC as a renewable and alternative power source have been recently utilized to power the MEC-Electro-Fenton process (see Fig. 4C). Zhang et al. [10] demonstrated the feasibility of using single chamber MFC to power a two-chamber MEC-Electro-Fenton system for recalcitrant pollutants treatment. The H_2O_2 production and pollutant degradation was improved by connecting 4 MFC reactors as power supply. This system has two key advantages: (1) electricity can be harvested by MFC without external electrical energy or additional chemicals; (2) the residual H_2O_2 removal as one of the key challenges in Fenton-like process, which can be easily monitored and in-situ removed by adjusting of the running mode [10]. The MFC powered MEC-Electro-Fenton systems could be one of the most promising technologies for the removal of organic pollutants and POPs in wastewater. However, several challenges still need to be addressed before industrial application. For example, the pollutant removal rate and current density are still low compared to conventional Electro-Fenton process. The current density and voltage applied to MEC could be enhanced by connecting several single chamber MFCs in series, but this method may not be feasible for long-term operation due to the voltage reversal [42], and the voltage applied to MEC also could not increase proportionally with the simply connecting MFCs in series [43]. Thus, more studies should be done to improve the voltage output of MFC and current of MEC in further work.

3.4. MFC powered Electro-Fenton system

MFC has been used to supply electric power to the Electro-Fenton system (see Fig. 4D) [9, 44, 45]. In this process, a single-chamber MFC was employed as a renewable electrical source to power the Electro-Fenton reaction for organic pollutants treatment. The power density is much higher than that achieved in two-chamber MFC-Electro-Fenton systems, allowing more efficient degradation of pollutants. Since no membrane is required, the single-chamber MFC could be an alternative power source of Electro-Fenton [46]. Such integration would save energy consumption and operation costs compared to the classical Electro-Fenton systems. However, the concentration of pollutant used was low, which also predicts poor performance for high concentration pollutants. The maximum mineralization efficiency was only 75% for 1 mM concentration of phenol. In another study, Zhang et al. [47] also modified one single MFC as power source to drive decolorization of 50 mg L⁻¹ of Methyl orange, the color removal efficiency could reach to 90.4% within 6 h. Nevertheless, the low voltage output of the MFCs is one key limitation for large-scale operation. Since the capacitor has great property for current storage [48], connecting a super capacitor in the current circuit could be an option to enhance the voltage input to the Fenton process in future work.

3.5. MREC-Electro-Fenton system

MREC as a novel hybrid bioelectrochemical system has been demonstrated as an efficient platform technology for H₂O₂ production [36]. In MREC, the electric energy generated by the exoelectrogens and salinity-gradient between different salt and fresh solutions were utilized to drive the H₂O₂ production and Fenton reaction. This system holds great potential as sustainable method to treat biodegradable matters in anode chamber and treat non-biodegradable pollutants in cathode

chamber without any external power supply. Li et al [11] have demonstrated the applicability of MREC-Fenton system for azo dye wastewater treatment (see Fig. 4E). The cost of treating Orange G wastewater was only 25.93 kWh kg⁻¹-TOC, which is much lower than of conventional electro-Fenton process with a cost of 45.8-865 kWh kg⁻¹ TOC [49, 50]. The key advantage of MREC-Fenton system is the replacement of electricity energy from power grid with renewable salinity-gradient energy which to directly drive the Fenton process. Due to that cathode and anode chamber are completely separated with RED stack, the continuous flow mode for wastewater in anode chamber does not affect the reaction of cathode. As a new technology, it is still facing several challenges. For example, the energy recovery still needs to be improved to make MREC-Fenton more efficient and competitive technology. Moreover, more cost-effective reactor configuration and large-scale operation could be the interest of further research for commercial application.

Table 2. is here.

4. Bio-anode used in bio-electro-Fenton systems

4.1. Anode materials

Since bio-electro-Fenton systems share the same anode reaction with MFCs and MECs, the cost-effective anode materials such as carbon fiber brush, graphite felt, carbon cloth, carbon mesh or activated carbon, which are capable of efficient electron transfer from bacteria to electrode in MFCs and MECs could be an ideal option for bio-electro-Fenton systems. So far, carbon fiber brush, carbon paper, carbon cloth and graphite felt have been tested in bio-electro-Fenton systems (Table 2). Most of the studies have not considered the anode materials and its modification as an objective. However, it is important to note the anode is an indispensable component, because exoelectrogens

growing on the surface of anode and transfer electrons to the electrode. It has been demonstrated in previous studies that an ideal anode material should have the following features: (a) strong biocompatibility and good electrical conductivity; (b) appropriate mechanical strength and toughness; (c) chemical stability and anti-corrosion; (d) high active surface area.

4.2. Microorganisms on the anode

As it is well known, the main feature of bioelectrochemical systems is the electrogenic microorganisms catalysed electron transfer from the organic matter to anodic electrode. The electrogenic microorganisms have been found in a wide variety of environments, such as domestic wastewater, municipal wastewater, brewery wastewater and anaerobic sewage sludge. A list of electrogenic microorganisms used in bio-electro-Fenton systems is shown in Table 2. The mixed-culture sources enriched from domestic wastewater and anaerobic sewage sludge have been used as inoculum in the most bio-electro-Fenton studies. The microorganisms on the anode have significant effect on the POPs removal in the bio-electro-Fenton system, which can increase the POPs degradation efficiency compared with the electro-Fenton system without microorganisms on anode under same operation conditions. For instance, Li et al [11] found the decolorization efficiency of Orange G reached about 88% in bio-electro-Fenton system with bio-anode, which was only 18% in electro-Fenton system with abiotic anode under same operation conditions. The mineralization of Orange G in terms of TOC removal showed similar trend as Orange G decolorization. When bio-electro-Fenton system was used to treat aniline wastewater, the aniline and TOC removal also have significant difference between the systems using abiotic anode and bio-anode (see the Fig.5). The improvement in the performance of mixed-culture bio-electro-Fenton systems requires great

understanding of the ecology in microbial communities. Nevertheless, there are few studies of the microbial communities on the anodes of bio-electro-Fenton systems. Microbial community composition of mixed culture is poorly defined in bio-electro-Fenton systems, and thus, there is a need to investigate the mechanistic and physiological behavior of microbes that can serve as model for developing for specific applications such as in situ production of H_2O_2 for POPs removal. In addition, an expansive diversity of exoelectrogenic microorganisms have been isolated and characterized, such as *Geobacter* species and *Shewanella* species [6], which may have the potential to generate more power densities compared to mixed culture due to the ability to oxidize the organic matter completely in anode chamber.

Fig. 5 is here

5. Main affecting parameters

The degradation efficiency of organic pollutants in the bio-electro-Fenton systems depends on operation parameters such as wastewater pH, cathode material, catalyst dosage, flow rate of air, cathode potential and initial pollutants concentration. Most of these parameters need to be optimized for achieving the best removal efficiency and lowest energy cost.

5.1. pH

With respect to the bio-electro-Fenton process, it has been found that acidic pH between 2 and 3 is important for degradation of pollutants in cathode chamber [10, 11, 57]. At high pH (≥ 4), the formation of ferrous/ferric hydroxide complexes led to the catalyst deactivation, which decreasing the quantity of $\cdot OH$. Thus, it requires an initial pH adjustment with acids and final neutralization of the treated water before it is released into the environment. However, when the pH is lower than 2,

the performance of pollutants degradation also would be inhibited. It could be due to the reaction of H_2O_2 with excessive H^+ to generate H_3O_2^+ , which is stable and difficult to react with Fe^{2+} to generate $\cdot\text{OH}$. For instance, Zhang et al. [10] reported that the maximum decolorization efficiency and TOC removal efficiency of methylene blue reached to 99.4% and 96% respectively at pH 3. When the pH was decreased to 1.5 or increased to 4, the decolorization efficiency and TOC removal efficiency decrease obviously. In general, the anodic reactions are proton producing whilst cathodic reactions are proton consuming in bioelectrochemical system. The accumulation of protons due to the slow and insufficient protons diffusion through membrane would cause a decrease of pH in anode chamber. Nevertheless, due to the consumption of H^+ at cathode, if no extra pH control was implemented, the pH of catholyte would increase to over 7 with the Fenton reaction. When the pH increase above 4, the Fe^{3+} species might precipitate as $\text{Fe}(\text{OH})_3$, which could diminish the amount of catalyst Fe^{2+} in the solution and break down H_2O_2 into O_2 and H_2O . Thus, pH would be one of the most important parameters. Recently, in order to reduce the cost of the pH adjustment, several studies have also demonstrated that composite cathodes have the advantages to self-regulate the supply of Fe^{2+} under neutral condition (Table 2).

5.2. Cathode material

The distinct advantages of bio-electro-Fenton process are the in situ electrochemical production of H_2O_2 via the oxygen reduction reaction and the pollutants degradation at the cathode. Among the bio-electro-Fenton reaction, H_2O_2 generation plays a decisive role and is affected by the types and properties of cathode materials [70]. To improve the oxygen reduction reaction activity, various carbonaceous materials have been widely tested as cathodes, including carbon felt [7, 57], graphite

[10, 24], gas-diffusion electrodes [8, 70], composite FePc/CNT/SS316 Cathode [66] and so on. The carbon-felt has a high specific surface that favors the fast generation of both components of the Fenton's reagent, and then $\cdot\text{OH}$ is produced from Fenton's reaction without significant H_2O_2 accumulation (Fig.6A). Gas-diffusion electrodes are preferred for H_2O_2 production with low cost and easy handling as no needs of energy consumption on aeration. This type of processes extends the acceptable pH range and increases the conversion efficiency of H_2O_2 to $\cdot\text{OH}$. Three-dimensional carbonaceous materials possess a large number of active surface sites leading to a very fast oxygen reduction and accumulation of H_2O_2 . It has been demonstrated that the cathode material should have the following characteristics: (a) good mechanical stability and electrical conductivity; (b) high surface areas; (c) can provide redox reaction sites and excellent electrolytic efficiency; (d) relatively low cost [71]. Some new types of carbon materials, such as plain graphene and oxidized graphene, have been demonstrated as one promising cathode material for H_2O_2 production in MFC [39], they could be potential cathode material in bio-electro-Fenton systems.

Some of the key drawbacks of classical Fenton process are the use of amounts of iron with further formation of iron sludge that must be removed and properly treated at the end of Fenton treatment, and need of acidification and subsequent neutralization [72]. Fe-functionalized carbonaceous cathode materials are the most widely studied functionalized cathode materials for Electro-Fenton system due to their high capacity for the in-situ production of large quantities of H_2O_2 production. Three-dimensional carbonaceous materials, such as carbon felt, active carbon felt, graphite felt and carbon-PTFE O_2 diffusion electrode are the most widely used material for the preparation of Fe-functionalized carbonaceous cathode. Several Fe-functionalized carbonaceous cathodes, such as Carbon felt/ γ -FeOOH [16], Fe@Fe₂O₃/graphite [17], Fe@Fe₂O₃/NCF [18], CNT/ γ -FeOOH [29],

Fe₂O₃/active carbon felt [53] and Fe@Fe₂O₃/carbon felt [63], have been successfully used as cathode to treat pollutants-contained wastewater at neutral pH (Table 2). These electrodes could serve as a solid Fe²⁺ source to avoid any excessive use of acids to adjust pH and to accelerate the cycling rate of Fe³⁺ reduced to Fe²⁺ (Eq. 4) (Fig.6B). The mechanism of the [•]OH generation depends on the properties of the solid iron source loaded on the cathode and the working pH of the wastewater in cathode chamber. This kind of bio-electro-Fenton process belongs to heterogeneous electro-Fenton process. Recently, some novel cost-efficient composite cathodes, such as Fe₂O₃/bentonite, Fe/bentonite [73], FeOOH/graphite and Fe₂O₃/graphite [74], have attractive increasing attention due to its merits of high H₂O₂ productivity and efficient Electro-Fenton activity. They could also be used as potential cathode of bio-electro-Fenton systems.

Fig. 6 is here

5.3. Catalyst dosage

Considering that the H₂O₂ production rate and yield could be constant at defined conditions in bioelectrochemical system, Fe²⁺ as catalyst could be a key factor for the final treatment performance [67]. According to the reaction of Fe²⁺ and H₂O₂ for [•]OH generation (Eq. 3), recalcitrant organics removal could increase with the increasing of Fe²⁺ concentration. However, the Fe²⁺ cannot be added without any limitation. The excessive Fe²⁺ would cause [•]OH loss (Eq. 5), and thus lead to gradual drop of degradation efficiency of pollutant [2]. In order to obtain maximum [•]OH production rate, the optimal Fe²⁺ concentration should be examined. For example, the optimal degradation efficiency (almost 100%) of azo dye could be obtained at 1.0 mM of Fe²⁺ in MFC-Electro-Fenton system, while further increasing of the Fe²⁺ concentration to 5 mM decreased degradation efficiency

to 80.15% [22]. Beside treatment performance, excessive Fe^{2+} addition will also add the operational costs [57]. Furthermore, excessive Fe^{2+} concentration would result in a large volume of sludge generation, which needs subsequent sludge treatment processes. Thus, similar to traditional Fenton reaction, the maximum removal of pollutants in bio-electro-Fenton process should be optimized in respect to Fe^{2+} concentration.

Due to the fact that soluble Fe^{3+} can be reduced to Fe^{2+} in cathode via reaction Eq. 4, some solid iron oxides such as $\alpha\text{-FeOOH}$, FeO , Fe_3O_4 , Fe_2O_3 have been investigated as iron catalysts in Electro-Fenton process [71]. The POPs removal efficiency was related to how good of the ability of iron oxides to release Fe^{2+} into the solution for catalyzing the Fenton's reaction (Fig.6C). Furthermore, synthetic iron/iron-containing nanoparticles have also been investigated for the Electro-Fenton treatment of POPs, e.g., nano- Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Pd/Fe}_3\text{O}_4$ [71]. These catalysts could also be used in bio-electro-Fenton system, which would be interesting for future studies on the system optimization. Recently, Tao et al. have demonstrated that the $\alpha\text{-FeOOH}$ can be used as catalyst in bio-electro-Fenton system to remove p-nitrophenol [57]. Up to 96% of p-nitrophenol (0.25 mM) was removed in 6 h under optimal conditions. The mechanism of p-nitrophenol removal was by the $\cdot\text{OH}$ generated from the reaction of H_2O_2 and Fe^{2+} which come from the partial dissolution of $\alpha\text{-FeOOH}$.

5.4. The membrane

Usually, bio-electro-Fenton system exploits an ion exchange membrane to separate the compartments of the cathode and anode. The most important function of a membrane is to assure a stable environment for bacteria growth and prevent the $\cdot\text{OH}$ and pollutants transferred from cathode to anode. At present, the most popular membranes used in bioelectrochemical systems are proton exchange membrane (PEM) anion exchange membrane (AEM) and cation exchange membrane (CEM). The PEM was designed to transfer H^+ , which can be used to induce a pH increase in the anode chamber and drop in the cathode chamber. However, the high cost (around \$3200/m², Ion power Inc., USA) would limit its use in commercial. The major drawback for AEM is the substrate crossover from the anode chamber to the cathode chamber because of the substantial concentration gradient. So far, most of the bio-electro-Fenton systems use cation exchange membrane (CEM) as a separator, but it has difficulty to maintain low pH in cathode chamber and thus may cause inhibition on the Fenton process. The pH rise could also cause extensive iron precipitation, which in return may damage the CEM and cathode. A bio-electro-Fenton system that can treat real and high concentration wastewater without causing pH issues is needed. Bipolar membrane typically consists of an anionic and cationic selective layer stacked in series. It leads to the simultaneous transport of protons to the cathode and hydroxide ions to the anode to balance charge. Our previous study has demonstrated that the bipolar membrane could be used to help sustaining a lower catholyte pH without the need of extra acid dosage in MEC-Electro-Fenton system for aniline removal [12].

5.4. The initial concentration of pollutants

The concentration of pollutants in cathode chamber is an important parameter directly affecting the degradation efficiency. Most of the bio-electro-Fenton systems could only obtain high treatment

efficiently with low concentration pollutants (Table 2). Moreover, the increase in initial pollutant concentration always leads to lower pollutant degradation efficiency and prolongs the degradation time. For instance, in MFC-Electro-Fenton system with carbon material as cathode, 100% degradation efficiency was obtained with 25 mg L⁻¹ amaranth azo dye, while the degradation efficiency decreased to 75.65% when the concentration of amaranth increased to 75 mg L⁻¹ [22]. Tao et al. [57] also found the degradation of p-nitrophenol decreased from 96% to 63% with the concentration increasing from 0.25 mM to 25 mM. In addition, 100% degradation of Orange G azo dye has been reported with initial dye concentration of 100-400 mg L⁻¹ of in MREC-Electro-Fenton system. However, the degradation efficiency was only 94.4% when the initial azo dye concentration was further increased to 500 mg L⁻¹ [11]. The reason for this phenomenon could be the low production yield of H₂O₂ and pH increasing with reaction in bioelectrochemical systems, which was insufficient to degrade high concentration pollutants. These findings implied that bio-electro-Fenton system need to be further developed to treat relatively high concentrations of organic pollutants before commercial application.

5.5. The cathode potential

The cathode potential is another important operational parameter for pollutant degradation rate and efficiency. In the first case, optimized cathode potential is usually chosen to attain the maximum H₂O₂ production rate and yield, and its value quite depends on the cathode material used. For example, the optimized cathode potentials reported so far was -0.4 ~ -0.5 V (vs. SCE) Graphite cathode [27, 36], -0.85 V (vs. SCE) for Graphite particle cathode [23], and -1.6 V (vs. Ag/AgCl) for carbon black graphite hybrid cathode, respectively [32]. It has been observed that the cathode potential could significantly affect the degradation of pollutants. As an example, Fu et al. [22]

shown that cathode potential in MFC-Electro-Fenton system was affected by the different external resistance and it would drop rapidly with the degrading of azo dye amaranth. In MEC-Electro-Fenton system, the cathode potential was affected by the applied voltage. Li et al. [12] reported the optimized cathode (Graphite cathode) potential for Fenton reaction was $0.45 \pm 0.01\text{V}$ (vs. SCE) at applied voltage of 0.5 V, which is in the range of optimized cathode potentials for H_2O_2 production with graphite cathode. In future work, enhance the current under optimized cathode potential would be one of the emphases for research.

5.6. The air flow rate

Oxygen is the electron acceptor on the cathode surface for H_2O_2 production. High air flow rate could enhance the dissolved oxygen in solution and promote the oxygen mass transfer rate, and thus, is beneficial for H_2O_2 production and accumulation in bioelectrochemical systems. However, extremely high air flow rates are not recommended since they may cause several problems in operation such as: excessive air supply could cause decrease in H_2O_2 accumulation [36, 53]. Meanwhile, the excessive high air flow rate could also disturb the mass transfer between catholyte and electrode and lead to a low catalytic efficiency for pollutants degradation by the Fenton process. Moreover, the air flow rates could also affect the energy consumption in terms of pumping, and thus, setting an optimal air flow rate is important for commercial application.

Compared to energy-intensive aeration, passive O_2 diffusion from air to gas diffusion cathode was more energy-saving method to produce H_2O_2 in bioelectrochemical systems. The H_2O_2 concentration could reach to 1300 mg L^{-1} with production rate of $1.9 \pm 0.2\text{ kg-H}_2\text{O}_2\text{ m}^{-3}\text{ d}^{-1}$ in MEC equipped with gas diffusion cathode [8]. The energy consumption only was $0.93\text{ kWh kg}^{-1}\text{-H}_2\text{O}_2$.

Several studies also demonstrated the passive O_2 diffusion using gas diffusion cathode was more efficient for H_2O_2 production in bioelectrochemical systems [27, 31]. Therefore, bio-electro-Fenton system equipped with gas diffusion cathode could be interest of future study. However, the mass transport of O_2 to the cathode would be limited under passive O_2 diffusion conditions, and thus slow down the H_2O_2 production rate. To overcome this limitation, the gas diffusion cathode with optimal catalytic activity for H_2O_2 production needs to be explored.

5.7. The current or current density

Current or current density is one of key parameters in bio-electro-Fenton systems since it regulates the amount of $\cdot OH$ produced. In the MFC-Electro-Fenton system, the external load could directly influence the current and $\cdot OH$ production, and further affect the abatement of POPs in cathode chamber. For example, Tao and coworkers studied the influence of external load of MFC-Electro-Fenton system from 20 to 1000 Ω on p-nitrophenol removal, and found that the maximum removal efficiency was achieved at 20 Ω and with the corresponding current of 0.653 mA [57]. Zhang et al. [61] also investigated the effect of current density by connecting different external resistances in MFC-Electro-Fenton system. When the external resistance decreased from 1000 to 20 Ω , the average current density increased from 327 ± 18 to 2383.33 ± 212.13 mA m^{-2} . The maximum paracetamol degradation efficiency was also observed at 20 Ω . In MEC-Electro-Fenton system, the current is supplied by external power supply or other power source such as MFC. In general, the rate of pollutants degradation increases with the increasing current since more H_2O_2 are formed at a given time. However, the current cannot be increased indefinitely since the cathode potential would be changed by the applied voltage, resulting in the side reactions, and thereby decreasing current efficiency and pollutants removal efficiency. The side reactions can involve: (i) high current density

by adding high external voltage would enhance the H_2O_2 electrochemical reduction through Eq. (6) [2, 30, 72], (ii) the H_2O_2 reaction with Fe^{3+} via Eq. (7) and (8) [22, 72], (iii) the destruction of $\cdot\text{OH}$ with H_2O_2 and Fe^{2+} via Eq. (9) and (5) [54, 56, 57].

To choose an optimal current or current density, the current efficiency should be considered as an important evaluation parameter. The mineralization current efficiency (MCE) is used widely to determine the current efficiency of single pollutant solutions. The MCE at a given operation time in batch mode is calculated from Eq. (9).

$$\text{MCE}(\%) = \frac{\Delta\text{TOC } n F V_s}{4.32 \times 10^7 m I t} \quad (9)$$

where ΔTOC is the experimental TOC abatement (in mg L^{-1}), n is the theoretical number of electrons exchanged in the mineralization process of the pollutant, F is the Faraday constant (96485 C mol^{-1}), V_s is the solution volume (in L), 4.32×10^7 is a conversion factor to homogenize the units ($3600 \text{ s h}^{-1} \times 12000 \text{ mg mol}^{-1}$), m is the number of carbon atoms of the molecule under study, I is the current (in A) and t is the reaction time (in h) [2, 72].

6. Environmental applications

Bio-electro-Fenton technologies are being developed to remove POPs from wastewater with the objective of aquatic environment protection and reuse of water. Table 2 summarizes the organic compounds that have been treated by the technologies. In bioelectrochemical systems, various of

biodegradable organic matters can be oxidized by the exoelectrogenic bacteria on the anode. Several previous reviews have extensively summarized the wastewater substrates that could be removed in anode chamber of bioelectrochemical systems [75, 76]. This work mainly reviews the POPs which can be degraded in the cathode chamber by the bio-electro-Fenton process. In accordance with this classification, this section will analyze the degradative behavior of pharmaceuticals, dyestuffs and some other industrial pollutants.

6.1. Pharmaceutical wastewaters

Over the past years, pharmaceutical wastewater is typically co-treated with municipal wastewater and it is responsible for a significant input of pharmaceuticals into sewage treatment plants [75, 76]. Conventional wastewater treatment plants provide very inefficient destruction of pharmaceuticals because they are usually resistant to biodegradation [2, 68]. Several pharmaceutical pollutants such as 17β -estradiol, 17α -ethynyl-estradiol, sulfadimidine, paracetamol [61], Ketoprofen, Diclofenac, Ibuprofen, Naproxen [62] and estrone have been tested for their degradability in the cathode of bio-electro-Fenton system. Xu et al. [18] demonstrated 81% of 17β -estradiol and 56% of 17α -ethynyl-estradiol removal in MFC equipped with $\text{Fe}@\text{Fe}_2\text{O}_3/\text{NCF}$ cathode (Fig. 7). The external resistance was the key affecting factor on 17β -estradiol removal. When the external resistance was equal to the internal resistance of the system, 17β -estradiol removal could reach over 90% under various pH values (2-7) of the catholyte [19]. The removal of estrone and sulfadimidine in MFC-Electro-Fenton system has been recently demonstrated [54]. In continuous mode, the removal efficiencies for estrone and sulfadimidine could reach 100% and 97%, respectively. Real medicinal herbs

wastewater treatment has also been investigated using MFC-Electro-Fenton system. The maximum COD removal of 84.02% was achieved under optimal conditions [68].

Fig.7 is here.

6.2. Dyes

Dyes materials constitute an important portion of wastewater effluent, most are non-biodegradable and show a relatively high persistence in soils and aquatic systems. Azo dyes account for over 60% of the total number of known dye structures, among which salicylic acid derivatives of mordant azo dyes are numerically predominant. The azo dyes could be decolorized completely in MFC [14, 78] and MFC-MEC coupled system [79]. However, the color disappearing was only due to the cleavage of azo bond, the mineralization was not as efficient as that of depolarization. For example, the Methyl orange was cleaved into sulfanilic acid and *N*, *N*-dimethylaniline and sodium sulfanilate [80] or *N*, *N*-dimethyl-*p*-phenylenediamine [81]. However, these by-products are not friendly to the environment. Many previous studies have demonstrated the capability of bio-electro-Fenton process to completely degrade and mineralize azo dyes, such as methylene blue, orange G, lissamine green B, crystal violet, orange II, amaranth and so on (Table 2). For instance, the azo bond of orange II could be cleaved by the electrochemical reaction in the cathode chamber. However, the further mineralization of intermediates derived from electrochemical reduction could only be completed by the electro-Fenton reaction in the cathode chamber (Fig.8) [22]. Since some azo dyes could also be used as electron acceptors in cathode, *e.g.*, Acid Orange 7 [79], Orange G [11], the current density would increase with the increasing of azo dyes concentration during the decolorize stage. Higher current density would be beneficial for the degradation of azo dyes [11]. In addition, higher organic

contents would lead to higher current efficiency with smaller energy consumption but requiring longer time for attaining acceptable mineralization degrees [13]. In general, the bio-electro-Fenton technology is more promising than non-Fenton bioelectrochemistry technology to degrade dyes from practical perspective.

Fig.8 is here.

6.3. Other industrial pollutants

The bio-electro-Fenton systems have been applied to remediate some synthetic wastewaters containing industrial pollutants (Table 2). The main purpose of these studies was to demonstrate the feasibility of pollutants degradation. For example, P-nitrophenol is widely used in the manufacturing of pesticides, pharmaceuticals, herbicides, explosives, dyes and other chemical industries [82-84]. Considering the toxicity and carcinogenicity, the p-nitrophenol contained wastewater is categorized as hazardous waste. The MFC-Electro-Fenton process has been applied to degrade the p-nitrophenol attributing to the oxidation by $\cdot\text{OH}$ [7, 57, 59]. The p-nitrophenol at concentration of 1 mM was firstly degraded into carboxyl acids, and then mineralized into H_2O and CO_2 [7]. When using the limonite as the Fe^{2+} source, the iron resource cost was only 0.03 Euro per Kg L^{-1} p-nitrophenol [57]. The triphenyltin chloride (TPTC) as one of the most intensively used organotin is toxic, bio-refractory and difficult to be degraded under natural conditions due to the high stability of Sn-C bond. Yong et al. [17] investigated the feasibility of TPTC removal in MFC-Electro-Fenton process, where the maximum TPTC degradation efficiency was 78.96% for initial TPTC concentration of $100 \mu\text{mol L}^{-1}$. However, the removal was significantly decreased to 42.35% when the initial TPTC concentration increased to $400 \mu\text{mol L}^{-1}$. With long oxidation times, the

diphenyltin (DPT) and monophenyltin (MPT) as intermediates were completely mineralized to inorganic Tin and CO₂ (Fig.9). Arsenite as one of typical carcinogen has serious threat to human health, which can be found in some regions groundwater [83]. Wang et al. investigated the feasibility of As(III) oxidation in MFC-Electro-Fenton system under neutral pH conditions [16]. The As(III) was effectively oxidized into As(V) by the [•]OH. However, the As(V) still remained in the aqueous solution. Thus, it still is a challenge to improve the removal efficiency and oxidation efficiency of As(III) in the MFC-Electro-Fenton system.

Fig.9 is here.

6.4. Treatment of real wastewaters

Landfill leachate can reach the adjacent surface and groundwater, which could cause potentially serious hazards on the surrounding environment and public human health [65]. Landfill leachate has been used as anodic substrate in MFCs and MECs, but the current density, coulombic efficiency and COD removal were quite low owing to huge portion of POPs [76]. Ganesh and Jambeck [85] applied an air cathode MFC treat real landfill leachate with $12033 \pm 3974 \text{ mg L}^{-1}$ COD, only obtained current density of 26.8 mA m^{-2} with CE of 6.9% and COD removal of 28%. MFC-Electro-Fenton system also has been applied to treat landfill leachate using pyrrhotite-coated graphite cathode [64]. The landfill leachate was characterized with COD of 1022 mg L^{-1} and BOD₅/COD ratio of 0.18. Color and COD removal efficiency of 77% and 78% was achieved after 45 days treatment, respectively. The treatment performance in MFC-Electro-Fenton system is better than of MFC. The research results indicated that the old-aged landfill leachate could be treated by MFC-Electro-Fenton's reaction using pyrrhotite cathode. As no commercial extra reagent was needed, this

process was economical and effective. Most recently, bio-electro-Fenton system was evaluated as post-treatment of an anammox system to treat landfill leachate [86, 87], the effluent with COD of $2401 \pm 562 \text{ mg L}^{-1}$ and BOD_5 of $237 \pm 57 \text{ mg L}^{-1}$ from anammox reactor were fed in anode and cathode chamber with loop recirculation, a maximum anodic COD removal of $1077 \pm 60 \text{ mg L}^{-1}\text{d}^{-1}$ with COD removal of 65% and cathodic removal rate of $897 \pm 200 \text{ mg L}^{-1}\text{d}^{-1}$ with COD removal of 45% was achieved. These results demonstrated that the bio-electro-Fenton system were integrated with conventional techniques will has practicable value in the field of engineering application.

Swine wastewater is one kind of complex wastewater, which could be biodegraded in anode chamber of MFC and MEC [75]. However, it also contains some complex compounds which could not be completely removed in the anode chamber. Xu et al. [63] coupled the anodic biodegradation and cathodic Fenton for enhanced swine wastewater treatment in MFC-Electro-Fenton system. In their study, swine wastewater with COD of 1652 mg L^{-1} , $\text{NH}_3\text{-N}$ of 378 mg L^{-1} and BOD_5 of 372 mg L^{-1} was first biodegraded in the anode chamber, where 46.5% of COD, 58.7% of $\text{NH}_3\text{-N}$, 71.7% of BOD_5 and 38.4% of TOC were removed at organic loading rate (OLR) of $4.6 \text{ g COD L}^{-1} \text{ d}^{-1}$. Subsequently, the anode effluent was continuously flowed into the cathode chamber, where the COD, $\text{NH}_3\text{-N}$, BOD_5 and TOC removal reached to 76.7%, 88.5%, 92.3% and 95.7%, respectively.

7. Challenges and Outlook

The bio-electro-Fenton systems are suitable for the treatment of wastewater containing POPs. However, some limitations and technical drawbacks still need to be addressed, which are listed as following: (i) high cost of the materials used to construct these systems, such as the electrodes and membranes; (ii) the current density and the removal efficiency of POPs are still low for scaling up; (iii) an iron extraction system is required to remove residual iron from the treated wastewater, and

the requirement for pH adjustment before and after treatment, which may increase the costs of the system; (iv) sludge still can be formed due to the addition of iron catalysts, which require a further treatment of the effluent from cathode.

In order to accelerate the industrial application of bio-electro-Fenton systems, the following issues should be given priority for significant developments:

- (1). High cost of membrane is an aspect that must be considered in future studies. Exploration of new materials and their modifications should be continued to overcome the limitations of current membranes present in the system. For example, single porous ceramic membrane, ultrafiltration membrane and sulfonated polymer membrane are not only cost-effective but also have high potentiality for in situ H_2O_2 production, could be interesting for future studies on system optimization [15].
- (2). One of the key factors that limit the development of larger-scale bio-electro-Fenton systems is the cost and efficiency of cathode material. Future work should focus on the development of low cost cathode, which could be used in a wide range pH and with large surface area. The potential candidates could be three dimensional electrode and iron-graphite or iron-carbon composite electrode [19, 23, 28].
- (3). Electro-Fenton reactor configurations might be applicable in bio-electro-Fenton system for further development. Such as flow-through Electro-Fenton and photo-Electro-Fenton reactor configurations [88, 89], could be converted into novel and cost-effective bio-electro-Fenton reactor.
- (4). Modeling of bioelectrochemical systems including all the parameters could be used to predict the behavior and performance of wastewater treatment in different kind of reactors [90-92].

However, no report about the modeling of bio-electro-Fenton system is available, which should be concerned in future research.

- (5). The application scopes of bio-electro-Fenton systems could be further expanded, e.g., disinfection. The feasibility of disinfection of wetland effluent by using bioelectrochemical H_2O_2 production has been previously demonstrated [28]. Since the $\cdot OH$ has stronger ability of oxidation than H_2O_2 , bio-electro-Fenton systems may be more efficient for disinfection.
- (6). The capital and operation costs of bio-electro-Fenton systems could be two of the decisive economic factors for commercialization of the technologies for wastewater treatment [11, 93]. However, most publications are only focused on fundamental issues, the capital and operation costs are rarely reported. Therefore, the information of capital and operation costs should be accurately provided in future work. Detailed economic analyses are also essential to understand the benefits of the bio-electro-Fenton systems before commercial application.
- (7). Life cycle assessment (LCA) as the method of choice for various kinds of new technologies has been used to estimate the environmental performance of bioelectrochemical systems [94]. However, no LCA study on the bio-electro-Fenton systems has been reported so far. Considering the rapid growth in the research of bioelectrochemical systems together with wide range of applications, it is only a matter of time before these new technologies are scaled up. To avoid unintended consequences, LCA of optimized bio-electron-Fenton systems is required to evaluate this technology on commercial scale in future work.
- (8). The combination of the Electro-Fenton process with other technologies to try to increase efficiencies obtained by the single process is a hot research topic nowadays. It is important to increase the removal of POPs at very low concentrations. So, it also is especially important to

combine the bio-electro-Fenton systems with a secondary process, such as biological post-treatment.

8. Scaling-up and investment cost of bio-electro-Fenton system.

So far most bio-electro-Fenton system studies were conducted in lab scale, system scaling-up is necessary in order to evaluate the commercial application feasibility. Scale-up of MFC and MEC from batch experiments to pilot-scale for wastewater treatment in anode chamber has been reported, which could offer insights into the scaling-up of bio-electro-Fenton process [95-97]. Moreover, the anodic electrode arrangement strategies have significant influence on the wastewater treatment in lab and pilot-scale reactors [96, 98]. Nevertheless, the removal efficiency of POPs in pilot-scale bio-electro-Fenton system is still unknown. Furthermore, the reactor design is also a key factor to up-scaling. Aiming the scale up of this system presented above and exploiting more effective technology, systems for treating organic pollutants should be improved according to the following requirements in future study. Firstly, allowing the continuous in-situ production of H_2O_2 and catalytic regeneration of Fe^{2+} to avoid the chemical transport and storage, and to reduce the formation of sludge. Secondly, some new challenges with respect to the performance should be addressed. Especially, how to improve the performance and efficiency of reactor and reduce the capital costs of reactor and operation should be investigated. Thirdly, due to the chemical components of most real wastewaters are very complicated, the bio-electro-Fenton system should be extensively studied with real wastewater than synthetic wastewater.

9. Conclusions

The technical feasibility of bio-electro-Fenton systems to degrade various types of POPs has been proved by the achievement of high degradation rate, low energy consumptions and effective

removal. The advantages and disadvantages of different kinds of bio-electro-Fenton systems have been reviewed. The role of operational parameters within the framework has also been critically evaluated. Previous studies mainly focused on the application of bio-electro-Fenton systems for the remediation of synthetic wastewaters typically dye, pharmaceutical or industrial wastewaters at lab scale. In recent years, researchers have moved their focus on to real wastewaters in flow reactors. Despite these developments, there is a lack of information regarding the improvement of reactor design and scaling-up and commercial application in industrial level. Moreover, another interesting but complex work could be the assessment of the economic feasibility of bio-electro-Fenton systems. The investment costs, mainly related to bioelectrochemical systems and operational costs including electrical energy consumption and reagents and maintenance should be considered.

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Figure captions

Fig. 1. Major achievements towards bio-electro-Fenton systems.

Fig. 2. Schematic of MFC (a) and MEC (b) for H_2O_2 production.

Fig. 3. Schematic illustration of the working principle of typical bio-electro-Fenton system.

Fig. 4. Schematic of different bio-electro-Fenton systems. (left chamber: anode; right chamber: cathode; RED: reverse electrodialysis stack). (A) MFC-Electro-Fenton systems; (B) MEC-Electro-Fenton system; (C) MFC powered MEC-Electro-Fenton system; (D) MFC powered Electro-Fenton system; (E) MREC-Electro-Fenton system.

Fig. 5. Effect of bio-anode on the POPs removal in bio-electro-Fenton systems. The figure was redrawn based the data from Refs. [11, 12] for (A) and (B), respectively. (A): MREC-Electro-Fenton system; (B) MEC-Electro-Fenton system with 0.5V applied voltage.

Fig. 6. The proposed reaction mechanisms of bio-electro-Fenton's reaction on different cathode materials and catalysts.

Fig. 7. Schematic illustration of 17β -estradiol and 17α -ethynyl-estradiol removal in MFC-electro-Fenton system equipped with $\text{Fe}@\text{Fe}_2\text{O}_3/\text{NCF}$ cathode. Redrawn from Refs. [18].

Fig. 8. Schematic diagram of the bio-electro-Fenton system for Azo dye (Orange II) degradation. Redrawn from Refs. [22].

Fig. 9. Schematic diagram of the bio-electro-Fenton system for TPTC degradation. (TPTC: triphenyltin chloride; DPT: diphenyltin; MPT: monophenyltin). Redrawn from Refs. [17].

Table 1. Performance of H₂O₂ production in different bioelectrochemical systems.

Material	Cathode material	Cathode area	Cathode chamber volume	External voltage	Cathode potential	Gas flow rate	Current or Current density ^c	Operation time	H ₂ O ₂ concentration (mg L ⁻¹)	H ₂ O ₂ (mg cm ⁻²)
Carbon rod	Graphite rod	18.84 cm ²	70 mL	-	-0.25 V	40 mL min ⁻¹	-	12 h	78.85	0.0
Carbon felt	Graphite	15 cm ²	169 mL	-	-	-	18.41 Am ⁻³	24 h	196.5	0.0
Carbon plate	Carbon felt	12 cm ²	1000 mL	b	-0.2 V	-	-	-	~0.68	-
Carbon felt	Graphite felt	4 cm ²	13 mL	-	-	-	1.17 A m ⁻²	-	~13	-
Carbon brush	Graphene oxide	3.14 cm ²	7 mL	-	-0.4 V	-	5 A m ⁻²	1 h	273	0.0
Carbon rod	Graphite rod	185 cm ²	-	0.5 V	-	-	5.3 ± 10.7 Am ⁻²	8 h	~1300	0.8
Carbon brush	Graphite	50 cm ²	300 mL	a	-	10 mL min ⁻¹	2.4 Am ⁻²	16 h	439	0.1
Carbon felt	Graphite	16 cm ²	64 mL	0.5 V	-0.85 V	-	-	8 h	711.2	0.2
Carbon felt	Carbon cloth	100 cm ²	500 mL	-	-	-	3.5 Am ⁻² (c)	4 h	-	0.1
Carbon plate	Graphite	33 cm ²	70 mL	b	-1.7 V	860 mL min ⁻¹	7.7 ± 0.6 Am ⁻²	24 h	1447	0.1
Carbon felt	Graphite felt	25 cm ²	200 mL	0.4 V	-	-	-	6 h	22.1±2.42	0.0
Carbon fiber felt	Graphite	3.14 cm ²	5 mL	c	-	-	3.5 mA	21 h	700	0.0
Carbon brush	Graphite/carbon	7 cm ²	14 mL	b	-1.4 V	-	-	-	39.8±10.4	0.1
Carbon fiber	Air cathode	49 cm ²	18 mL	d	-	20 mL min ⁻¹	-	-	3100	-
Carbon fiber	Air cathode	31.4 cm ²	18 mL	d	-	-	3.73 Am ⁻²	-	3100±370	-
Carbon brush	Graphite plate	9 cm ²	40 mL	-	-0.48 V	12 mL min ⁻¹	1.43±0.09 Am ⁻²	72 h	778±11	0.0
Carbon fiber	Carbon cloth	79 cm ²	120 mL	-	-0.5 V	-	1 A m ⁻²	6 h	230	0.0

a: One MFC power the MEC.

b: Control the cathode potential using potentiostat. All the potentials were vs. Ag/AgCl reference electrode.

c: Control the current by a potentiostat.

d: Control the anode potential using potentiostat.

e: Watch different units.

:- No report the value in references

Table 2. Performance of pollutants degradation in different bio-electro-Fenton systems.

node material	Anodic inoculum	Cathode material	Membrane	Cathode chamber volume	Pollutants	Concentration	pH	Removal	Operati time
Carbon felt	<i>Shewanella decolorationis</i> S12	CNT ^b /PTFE/ γ -FeOOH	CEM	75.6 mL	Orange II	35 mg L ⁻¹	7	100%	43 h
Graphite	Anaerobic sludge	Graphite	PEM	250 mL	Acid blue 113	300 mg L ⁻¹	3	91.57%	-
Graphite	-	Graphite	PEM	70 mL	Amaranth	75 mg L ⁻¹	3	84.24%	2 h
Carbon felt	Brewery wastewater	Fe@Fe ₂ O ₃ /NCF ^a	GORE-TEX cloth	75 mL	Rhodamine B	15 mg L ⁻¹	3	95%	12 h
Graphite rod	<i>T. versicolor</i> <i>S. oneidensis</i>	Graphite rod	CEM	250 mL	Lissamine Green B	10 mg L ⁻¹	2	94%	9 h
					Crystal Violet	10 mg L ⁻¹	2	83%	
					Reactive Black 5	50 mg L ⁻¹		88.2%	15 mi
					Lissamine Green B	10 mg L ⁻¹		98.2%	15 mi
raphite sheet	Sewage sludge	Graphite sheet	-	150 mL	Crystal Violet	5 mg L ⁻¹	7.5	96.2%	15 mi
					Indigo Carmine	20 mg L ⁻¹		97.2%	15 mi
					Poly R-478	80 mg L ⁻¹		19.1%	15 mi
Carbon felt	<i>Shewanella decolorationis</i> S12	Ppy/AQDS/Carbon ^d	CEM	75 mL	Orange II	70 mg L ⁻¹	7	100%	50 h
Carbon cloth	Anaerobic sludge	Carbon felt	PEM	100 mL	Acid Orange 7	50 mg L ⁻¹	3	89%	60 h
Graphite fiber brush	Anaerobic sludge	Fe ₂ O ₃ /ACF ^e	CEM	550 mL	Methyl orange	5 mg L ⁻¹	3	86.7%	2 h
Graphite rod	-	Graphite rod	PEM	100 mL	Congo red	100 μ M	7	90%	72 h
Carbon felt	Domestic wastewater	FePc/CNT/SS316	PEM	130 mL	Reactive Black 5	50 mg L ⁻¹	-	80%	12 h
Graphite rod	Anaerobic sludge	Graphite rod	PEM	250 mL	Acid blue 113	100 mg L ⁻¹	3	71.36%	12 h
Carbon fiber brush	Domestic wastewater	Graphite	CEM and AEM	50 mL	Orange G	400 mg L ⁻¹	2	100%	10 h
Carbon fiber brush	Domestic wastewater	Graphite	BPM	250 mL	Methylene	50 mg L ⁻¹	3	97%	16 h
Carbon felt	Anaerobic sludge	Graphite plate	CEM	250 mL	Acid Orange 7	16 mg L ⁻¹	6	96.4%	2 h
Carbon felt	Anaerobic sludge	Carbon felt	AEM	300 mL	P-nitrophenol	139 mg L ⁻¹	3	100%	96 h
Carbon felt	Anaerobic sludge	Carbon felt	PEM	50 mL	P-nitrophenol	34.75 mg L ⁻¹	2	96%	6 h
Carbon fiber brush	-	Carbon felt	-	-	Phenol	94.1 mg L ⁻¹	3	95%	22 h
Carbon felt	Brewery wastewater	Fe@Fe ₂ O ₃ /Carbon felt	GORE-TEX cloth	75 mL	2-propanol	1200 mg L ⁻¹	3	-	72 h
Carbon felt	<i>Shewanella decolorationis</i> S12	Carbon felt	CEM	75.6 mL	2-nitrophenol	40 mg L ⁻¹	7	100%	30 h
Carbon felt	Anaerobic sludge	Fe@Fe ₂ O ₃ /NCF ^a	PEM	75 mL	17 β -estradiol	20 μ g L ⁻¹	3	81%	10 h
					17 α -ethynyl-estradiol	20 μ g L ⁻¹		56%	
Carbon felt	Anaerobic sludge	Fe@Fe ₂ O ₃ /NCF ^a	PEM	75 mL	17 β -estradiol	0.12 mg L ⁻¹	3	95%	6 h
					Bisphenol A	1 mg L ⁻¹		100%	
Graphite rod	Anaerobic sludge	Graphite	PEM	125 mL	Estrone	1 mg L ⁻¹	3	75%	24 h
					Sulfamethazine	1 mg L ⁻¹		98%	
					Triclocarban	1 mg L ⁻¹		97%	
Graphite felt	Anaerobic sludge	Graphite plate	PEM	216 mL	Paracetamol	10 mg L ⁻¹	2	70%	9 h
					Ketoprofen	40 μ g L ⁻¹		61%	
Carbon fiber brush	Domestic wastewater	Carbon felt	CEM	100 mL	Diclofenac	40 μ g L ⁻¹	2	97%	5 h
					Ibuprofen	40 μ g L ⁻¹		86%	
					Naproxen	40 μ g L ⁻¹		81%	

Carbon fiber brush	Domestic wastewater	Graphite	BPM	50 mL	Aniline wastewater	4512 mg L ⁻¹	3	98.3%	6 d
Graphite rod	Brewery wastewater	Fe@Fe ₂ O ₃ /Carbon felt	GORE-TEX cloth	450 mL	Swine wastewater	1652 ^c	3	95.7%	12 h
Carbon felt	Anaerobic sludge	Graphite sheet	CEM	250 mL	Landfill leachate	1022 ^c	5.4	78%	45 d
Carbon felt	Landfill leachate	Carbon felt	CEM	280 mL	Landfill leachate	2152±624 ^c	3	81%	-
Carbon felt	Dairy wastewater	Carbon felt	PEM	750 mL	Oily wastewater	3.7 mM	-	40%	4 h
Carbon felt	Dairy wastewater	Carbon felt	AEM	750 mL	Oily wastewater	878.2 ^c	3	77%	183 h
Graphite plate	Anaerobic sludge	Fe@Fe ₂ O ₃ /Graphite	PEM	450 mL	Herbs wastewater	6183±309 ^c	3	84.02%	50 h
Carbon felt	<i>Shewanella putrefaciens</i> SP200	Carbon/γ-FeOOH	CEM	75 mL	Arsenite	1 mg L ⁻¹	7	96%	72 h
Graphite felt	<i>S. oneidensis</i> MR-1	Fe@Fe ₂ O ₃ /Graphite	PEM	30 mL	Triphenyltin chloride	35.1 mg L ⁻¹	3	80.39%	100 h
Graphite plate	<i>S. cerevisiae</i>	Fe@Fe ₂ O ₃ /Graphite	PEM	500 mL	Glucose	500 mg L ⁻¹	3	68.81%	12 h

a: Non-catalyzed carbon felt. b: Carbon nanotube. c: COD (mg L⁻¹). d: polypyrrole/anthraquinone-2, 6-disulfonate modified carbon felt. e: active carbon felt. PEM: proton exchange membrane. CEM: cation exchange membrane. GORE-TEX cloth: an expanded polytetrafluoroethylene (e-PTFE) laminated cloth. CEM: Cation Exchange Membrane. BPM: bipolar membrane. No report in references

Highlights

- Review of bio-electro-Fenton technology for persistent organic pollutants removal.
- Recent advances in reactor design and key operational parameters are discussed.
- Insights into future research and technology development of bio-electro-Fenton.
- Challenges and prospects for commercial utilization are highlighted.
- Scaling-up and investment cost are two key issues need to be addressed in future.