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A Critical Review on Cathode Modification Methods for Efficient Electro-Fenton Degradation of Persistent Organic Pollutants

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Abstract

The Electro-Fenton (EF) technology has received significant research attention because of its efficacy in the degradation of persistent organic pollutants (POPs), which mainly relies on the *in-situ* generation of H_2O_2 via the 2-electron oxygen reduction reaction and the subsequent formation of •OH. However, the practical application of the EF technology still needs to deal with shortcomings such as the limited performance of the traditional heterogeneous catalyst and the restricted generation of •OH that could be overcome by performing modification on the cathode. This work reviewed the reported cathode modification methods including thermal and (electro)chemical treatment and modification based on materials such as metals, graphene, carbon nanotubes, and polymers. Furthermore, the documented performances of the EF systems with differently modified cathodes in degrading specific POPs were presented. Finally, the advantages and limitations of these cathode modification methods were discussed, and some research perspectives were proposed to improve the practicability and feasibility of the EF technology.

Keywords: Electro-Fenton; Hydrogen peroxide (H_2O_2); Modification methods; Modified cathodes; Persistent organic pollutants (POPs)

Nomenclature: 2, 4-dichlorophenoxyacetic acid, 2, 4-D; Acetylene black, AB; Actived carbon felt, ACF; Advanced oxidation processes, AOP; Anthraquinone, AQS; Aromatic organic pollutants, ArH; Boron-doped diamond, BDD; Carbon black, CB;

Carbon cloth, CC; Carbon felt, CF; Carbon felt modified by CB and PTFE, CP-CF; carbon fiber paper, CFP; carbon nanofibers, CNFs; carbon nanotubes, CNTs; chemical oxygen demand, COD; Ciprofloxacin, CIP; Composite cathode of polyaniline modified GF, PANi/6-GF; Current efficiency, CE; Cyclic voltammetry, CV; Electro-Fenton, EF; Energy consumption, EC; Enrofloxacin, ENR; Fe/Co/Zn-tri-metal co-doped carbon nanofibers, Fe/Co/Zn@C-NCNFs-800; gas diffusion electrode, GDE; graphene oxide, GO; graphite felt, GF; Graphite felt modified by CB and PTFE, CP-GF; Heterogeneous electro-Fenton, HEF; Levofloxacin, LEV; Metal-organic framework, MOF; Methylene blue, MB; mineralization current efficiency, MCE; Mn/Co metal-organic frameworks derivatives modified graphite felt, Mn_xCo_{3-x}@C-GF; Natural air diffusion electrode, NADE; Orange II, OII; Oxygen reduction reaction, ORR; Oxygen-containing functional groups, OGs; Oxytetracycline, OTC; Persistent organic pollutants, POPs; *p*-nitrophenol, *p*-NP; Polyacrylonitrile, PAN; Polyaniline, PANi; Polypyrrole, Ppy; Polytetrafluoroethylene, PTFE; Ratio of the peaks of D-band and G-band, I_D/I_G; Reduced graphene oxide, rGO; Rhodamine B, RhB; Saturated organic pollutants, RH; Spent coffee ground activated carbon, SAC; Sulfamethazine, SMT; Tetracycline, TC; Total organic carbon, TOC; Total phosphorus, TP; Triclosan, TCS; Zeolitic imidazolate framework-8, ZIF-8

1. Introduction

Since the water quality becomes increasingly poor, advanced oxidation processes (AOPs) that can efficiently remove and mineralize persistent organic pollutants (POPs)

have attracted tremendous attention from researchers [1]. AOPs are based on the *in-situ* production of highly reactive oxidizing agents such as superoxide radical anions ($O_2^{\bullet-}$), ozone (O_3), or hydroxyl radicals ($^{\bullet}OH$) that non-selectively react with all kinds of POPs [2]. As the representative AOP, the traditional Fenton process has been frequently applied to degrade various POPs including antibiotics, dye molecules, herbicides, pesticides, pharmaceuticals, phenolic compounds, and surfactants due to its powerful generation of $^{\bullet}OH$ [3]. The chief advantage of the traditional Fenton process is simplicity and high efficiency in operation, thus enabling its wide application in treating water and wastewater [4]. However, the traditional Fenton process also has significant downsides including the demand for added H_2O_2 solutions and catalysts which increases the treatment cost, the concomitant high corrosivity which might corrode the pools, and the difficulty of the treated wastewater to meet the discharge standard. As a result, electro-Fenton (EF) was introduced. EF is the superior process founded on the Fenton process with the advantages of i) the *in-situ* generation of H_2O_2 on the cathode in the presence of a small number of added catalysts (i.e., satisfactory cost-effectiveness) and ii) the guaranteed efficiency in degrading POPs [5, 6]. Nevertheless, the practical application of EF still needs to overcome limitations including the narrow optimum pH range. For example, at pH>4 Fe^{2+} as the catalyst will be lost in the form of $Fe(OH)_3$ by precipitation, leading to the subsequent treatment of the generated iron sludge [7].

Modified EF therefore needs to be developed to overcome these drawbacks [8]. To improve the performance of the EF system, some strategies have been proposed such as employing novel types of catalysts or performing modifications on the anodes and cathodes. However, catalysts tend to have serious aggregation problems and a low specific surface area, leading to limited catalytic activities, while modifying the anodes usually requires high costs [9]. Therefore, there is a burning desire to fabricate modified cathodes with the advantages of being environmentally friendly, earth-abundant, highly tunable, and electrochemically stable to optimize the EF system.

2. Basic Mechanisms of EF Process

Cathode modification should be based on the mechanisms of the EF process as illustrated in **Fig. 1**. The basics of the EF process combine electrochemistry and the classical Fenton reaction including the use of Fe^{2+} as the catalyst and H_2O_2 in the removal of POPs [10]. H_2O_2 electrochemically generated from oxygen (**Eq. 1**) is a type of weak oxidant that reacts with Fe^{2+} to form an unstable but strong oxidizing $^{\bullet}OH$ (**Eq. 2**), which is regarded as the core reaction of the EF process. At the surface of the cathode, the electrochemical recycle reactions between Fe^{2+} and Fe^{3+} (**Eqs. 2 and 3**) guarantee the continuous generation of $^{\bullet}OH$ [11-14]. As the high yield of H_2O_2 is required to render the essential $^{\bullet}OH$ species, the 2-electron oxygen reduction reaction (ORR) (i.e., **Eq. 1**) is the preferred reaction in EF pools. The 2-electron ORR to H_2O_2 therefore plays a vital role in decentralized applications such as wastewater

treatment [15] and groundwater remediation [16]. However, with the change in the solution pH and cathode materials, the 2-electron ORR could be accompanied by the competing 4-electron ORR (**Eq. 4**).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (4)$$

Novel cathodes should therefore be fabricated to provide high selectivity for the 2-electron ORR, which is highly relevant to EF. Consequently, the past decade has spared no efforts to develop new materials that can be applied to preferably produce H_2O_2 through the 2-electron ORR [17]. In spite of this considerable interest, the origin of selectivity has yet to be fully understood. In addition to selectivity issues, H_2O_2 could go through several reactions after its formation on the cathode [18]. First, H_2O_2 could be further electroreduced to H_2O via **Eq. 5** [19], especially on porous cathodes [20]. Second, H_2O_2 could be oxidized to O_2 on the anode with $HO_2^{\bullet}$ as an intermediate (**Eq. 6**) [19, 21]. Moreover, H_2O_2 might be disproportionated into O_2 and H_2O in a non-electrochemical bimolecular reaction (**Eq. 7**) [22]. Finally, the attack of ${}^{\bullet}OH$ on POPs like aromatic (ArH) and saturated (RH) organic pollutants could proceed via **Eqs. 8 and 9** [2]. Proper modifications of the cathodes are likely to strengthen the 2-electron ORR and weaken the 4-electron ORR and other side reactions. Thus, there

is an urgent need to develop and apply viable modification methods to obtain cathodes with high efficiency and selectivity for the EF technology [17], which is the focus of this review.

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \quad (5)$$

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \quad (6\text{-}1)$$

$$HO_2^{\bullet} \rightarrow O_2 + H^+ + e^- \quad (6\text{-}2)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (7)$$

$$ArH + {}^{\bullet}OH \rightarrow ArHOH^{\bullet} \quad (8)$$

$$RH + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}R \quad (9)$$

3. Methods for Cathode Modification

3.1 Thermal treatment

The thermal treatment is an efficient but uncomplicated method for felt modification where cathodes are annealed in a furnace fed with gas flow containing O and/or N [23, 24]. As shown in **Fig. 2**, this type of modification does enhance the hydrophilicity and electrochemical properties of felt electrodes [25, 26]. Based on the cyclic voltammetry (CV) curves, Le, et al. [26] concluded that the treated cathode after the thermal process achieved a larger current response compared to the raw one. The improved hydrophilicity and porous surface (**Fig. 2a-2d**) elevated the electron transfer efficiency, resulting in the expansion of the electroactive surface area on the cathode. Using the paracetamol as the targeted pollutant, 51.0% total organic carbon (TOC)

removal was observed for the porous carbon cathode after 2-h EF treatment in an acidic aqueous environment, compared to 20.0% TOC removal for the raw carbon felt (CF). It was particularly interesting that the TOC removal value reached 94.0% after 10 h treatment even though paracetamol is known as a refractory molecule [26].

In addition, the thermal treatment can introduce oxygen-containing functional groups (OGs) that promote the production of H_2O_2 on the cathode. OGs can make use of the defect sites in the carbon structure to improve their hydrophilic property and absorb oxygen, which enhances the electrical conductivity and the ORR activity and subsequently increases the production of H_2O_2 [27]. OGs could be introduced by annealing cathode materials and modified materials (KOH, CO_2, or CH_3COOH) together at a temperature of 800-1000 °C [28-30].

3.2 Chemical and electrochemical treatment

Recently, an effective chemical treatment that utilizes largely carbon black (CB) and polytetrafluoroethylene (PTFE) has been proposed. CB is a fine black powder that is the electro-active part in the cathode for electrochemical reduction of dissolved oxygen to H_2O_2 (**Eq. 1**). Since CB powder can't bind to CF itself, PTFE, a polymeric binder, can be used to strongly bind CB to CF. Increasing the percentage of PTFE will facilitate the generation of H_2O_2 and make the binding stronger [31]. Jiao, et al. [4] mixed CB with different weight percentages of PTFE in the mixture of CB and PTFE (denoted the weight percentage of PTFE as *p*) to optimize the composition of the

cathode. The performance of the modified CF was assessed using Orange II (OII) as the target pollutant. When the cathode was prepared at a *p* of 75.0%, the highest current efficiency (CE), removal efficiency and adsorption of OII were attained [4]. This finding was attributed to the balance between adsorption and H_2O_2 generation [31]. Similar results have been reported elsewhere. Wang, et al. [32] used the graphite felt (GF) coated with absolute ethanol and the mixture of PTFE/CB at a ratio of 0.6 to degrade sulfamethazine (SMT) in the EF process, and after 60 min the TOC removal efficiency was 39.7% under optimized conditions [32]. Cai, et al. [33] combined the GF modified by CB and PTFE (CP-GF) and a boron-doped diamond (BDD) anode to remove 2, 4-dichlorophenoxyacetic acid (2, 4-D). Compared to the pristine GF, using CP-GF as the cathode had higher mineralization current efficiency (MCE) and TOC removal with lower energy consumption (Ec). The mainly effective radical in EF was $^{\bullet}OH$, and it led to 92.0% 2, 4-D degradation [33]. Later, Cai, et al. [3] constructed a flow-through system also for 2, 4-D degradation using the CF modified by CB and PTFE (CP-CF) with high H_2O_2 yield as the cathode and boron and cobalt co-doped TiO_2 nanotubes as the anode for the first time [33, 34]. The novel system possessed more than 1.5 times the rate constant of 2, 4-D degradation, and realized the efficient and economical degradation of phenol, atrazine, SMT, methylene blue (MB), and *p*-nitrophenol (*p*-NP) [3].

CP-GF also proved to be effective in removing multiple contaminants from domestic sewage. Under the optimal condition, NH_3-N, total phosphorus (TP), and

chemical oxygen demand (COD) in domestic sewage could be efficiently removed, meeting the prescribed discharge standard in China (NH_3-N: 15 $mg \cdot L^{-1}$, TP: 0.5 $mg \cdot L^{-1}$, COD: 60 $mg \cdot L^{-1}$). In addition, the CP-GF cathode was able to perform well in H_2O_2 production and COD removal even after 10 cycle tests [35].

In a few cases, acetylene black (AB) could be used as a substitute for CB to modify the cathode materials. Tan, et al. [36] fabricated the AB-based gas diffusion electrode (GDE) modified with PTFE and coupled it with a PbO_2 anode to degrade isophorone. The high H_2O_2 concentration of 718.91 $mg \cdot L^{-1}$ was attained with lowest Ec and CE within 1 hour, leading to nearly complete removal of isophorone within 60 min [36].

The chemical treatment of cathodes also includes the use of chemicals such as HNO_3, KOH, and/or NaOH to activate the surface of GF materials. The GF samples could be firstly immersed in a hydrothermal synthesis reactor containing concentrated nitric acid and then heated at a suitable temperature for several hours to fabricate graphite felts with abundant chemisorbed oxygen on the surface [37]. After treatment, the samples need to be washed with ultrapure water until the pH of rinse water is neutral and then vacuum dried before being applied as electrodes. Previous studies have observed that the increase in acid concentration resulted in the improvement of the electrochemical performance of modified cathodes [38, 39]. Liu, et al. [40] used levofloxacin (LEV) as the target pollutants and observed that the ideal

HNO_3-modified GF exhibited a very high apparent degradation rate constant (0.40 min^{-1}) [40].

The combination of the chemical and thermal treatments could be effective in improving the electrochemical behavior of the GF electrodes [41]. This is because the modified cathode electrodes possess higher hydrophilicity, larger specific surface area, and more OGs. Lai, et al. [42] observed that the number of OGs like H–O–H, C–OH, –COOH, and C=O significantly increased on the surface of the GF modified by NaOH activation at 400 ℃. The complete destruction of oxytetracycline (OTC) was reached by applying NaOH-modified GF in the EF system after 60 s, which followed pseudo-first-order kinetics with the apparent rate constant of 1.20 min^{-1}. Moreover, the modified GF exhibited good stability during 5 cycle tests [42]. Recently, Zhang, et al. [43] first proposed a highly efficient dual-cathode EF process that combined one cathode modified by HNO_3 and a natural air diffusion electrode (NADE; CP-CF) [44]. The system was applied to treat organic wastewater at a wide range of pH (3-9) with economical Fe^{3+} as the homogeneous catalyst. The NADE acted as one cathode mainly for H_2O_2 generation without aeration while CF modified by nitric acid worked as the other cathode for Fe^{2+} regeneration [43]. For a variety of contaminants (bronopol, 2,4-D, SMT, and phenol), the highly efficient dual-cathode EF process achieved 48.0%-72.0% TOC removal within 60 min, which was 1.5-2.5 times higher than that of the conventional EF process. Besides, the system kept excellent contaminants removal efficiency after 10 cycle tests [43].

Some researchers found difficulty in controlling the oxidation degree owing to the presence of manifold operating conditions (e.g., temperature, reaction time, reagent concentration, and type of oxidant) when employing the chemical treatment [45]. The electrochemical treatment can be conducted in a controlled way through the easily adjustable treatment current and time and is therefore more environmentally friendly and practical [46, 47]. Consequently, the electrochemical treatment is an alternative for the introduction of OGs at the surface of CF [48]. Xu, et al. [49] modified the GF cathode via the anodic oxidation process in the NH_4HCO_3 aqueous solution and exhibited the electro-generation of H_2O_2 by the modified cathode in the EF system. After the modification, the number of beneficial functional groups such as C=O and COO has remarkably risen, which resulted in the enhancement of kinetics of ORR and the increase of H_2O_2 production and Ec to 2.00 $mg \cdot h^{-1} \cdot cm^{-2}$ and 42.4%, respectively. During 5 cycle tests, the modified cathode maintained stable electrochemical syntheses of H_2O_2 that was favorable for the removal and mineralization of POPs [49]. Low-cost chemical reagents like H_2SO_4, NH_4HCO_3, or NaOH aqueous solutions were applied as the electrolyte to construct defects for electrochemically modified GF as well. According to the Raman spectra of structural defects on the surface of GF, it was demonstrated that GF anodized by H_2SO_4 performed best in promoting the *in-situ* generation of H_2O_2. The higher ratio of the main peaks of D-band and G-band (I_D/I_G) corresponds to the higher H_2O_2 productivity, which demonstrated the positive influence of defects made for the accumulation of

H_2O_2 via the 2-electron ORR [50-52]. When it was employed for rhodamine B (RhB) degradation, more than 99.0% absorbancy removal was observed within 30 min. The results also showed that after 5 cycle tests, the modified GF maintained stability and reusability (i.e., 99.0% removal of the absorbancy of RhB after 30 min and over 80.0% TOC removal in 100 min). Meanwhile, the modified GF was effective for other model pollutants like MB (81.5% TOC removal) and OII (78.6% TOC removal) [50]. Dong, et al. [53] used similar methods of modifying the pristine GF and focused on the effect of different treatment times on electrode performance. Considering the Ec and H_2O_2 yield, 5 min was chosen as the best modification time. Compared with bare GF cathode, the higher current response and the more excellent cycling stability were achieved with the improved GF cathode. These results showed that electrochemical modification is an efficient technology to enhanace the H_2O_2 yield on optimized GF cathodes and can therefore improve the TOC removal in the EF process [53].

3.3 Metallic treatment

Metallic modification aims to enhance the conductivity of cathode materials, thus leading to higher degradation rates of targeted contaminants. Generally, metals are coated on the surface of cathodes through impregnation with solutions containing metallic ions such as Fe^{2+}, Co^{2+}, Cu^{2+}, and Mn^{2+}. The performances of modified cathodes reported in recent years are summarized in **Table 1**. Often, the cathodes were modified via an *in-situ* solvothermal process applying a Teflon lining autoclave containing the mixture solution of effectual chemicals [54]. For example, the

calculated weight difference (i.e., 0.15 g) of every CF after thermal treatment could indicate that Fe atoms have adhered to the surface of CF [7]. This statement was supported by the scanning electron microscopy and energy dispersive X-ray spectroscopy analyses on the morphology of the prepared cathode after being immersed in the solution containing NH_4F (125 mM), $Co(NH_2)_2$ (0.5 M), $FeSO_4 \cdot 7H_2O$ (25 mM), and $Fe(NO_3)_3 \cdot 9H_2O$ (12.5 mM) at about 100 °C [55, 56]. In addition, the content of Fe2p analyzed by X-ray photoelectron spectroscopy increased from 0.9% to 4.4%, indicating the successful modification to the pristine CF. To further explore the electrocatalytic activity of the modified cathode, Yang, et al. [7] used ofloxacin as the targeted pollutant and attained complete TOC removal after 8 h. Surprisingly, the modified CF even showed excellent reusability with about 84.0% TOC degradation observed even after 6 cycle tests. This modified cathode even solved the major challenge of the narrow applicable pH range because the surface catalyzed process occurred at the solid-liquid interface and curbed the formation of $Fe(OH)_3$ precipitation. Significant removal rates of heterogeneous EF (HEF) were achieved with the modified CF at pH=7 [7]. Chu, et al. [57] used lab-synthesized FeS_2 as the main components to prepare the modified cathode FeS_2/CF. The noted high electrocatalytic activity and remarkable efficiency resulted from the high cumulative concentration of $^{\bullet}OH$ after 20 min. At the wide pH of 3-9, >80.0% anthracene was eliminated outclassing that in the electrochemical system with the raw CF [57].

The growth of metal materials on the surface of the cathode can also be carried out by other treatments including direct calcination. The performance of the modified cathode is associated with the different loading concentrations of metals. Tang, et al. [58] immersed the carbon cloth (CC) in different concentrations of $FeCl_3 \cdot 6H_2O$ ethanol solution and the degradation efficiency of tetracycline (TC) went up initially, and then decreased with the increase of the FeOCl amount. In addition, when the FeOCl/CC was coupled with the other cathode activated by KOH for more H_2O_2 generation, the EF system was featured with a high TC degradation rate (96.0% in 20 min), >95.0% TC removal in the wide pH range (3-7) in 30 min, high stability, a high oxidative flux (1510 $mg \cdot min^{-1} \cdot m^{-2}$), and a low Ec (45 $kWh \cdot kg^{-1} \cdot COD^{-1}$) [58].

The metals can also be electrodeposited on the cathode materials. Dong, et al. [59] electrodeposited MnO_2 on the carbon fiber paper (CFP) substrate. In addition to a low specific Ec of 6.9 $kWh \cdot kg^{-1} \cdot COD^{-1}$, high TOC and COD removal after 4 h (65.2% and 74.8%, respectively) were attained in the EF treatment of shale gas fracturing flow-back wastewater. The residual COD level met the requirement of the integrated wastewater discharge standard.

3.4 Graphene-based modification

Graphene has been a hot topic lately in material sciences for its remarkable electrical/mechanical/optical/physical/thermal properties and a high specific surface area [60, 61]. Therefore, graphene has been widely used for increasing the

electrochemical activity of electrodes [62]. Recently reported graphene-based modifications in the EF process for the removal of various contaminants are summarized in **Table 2**. Different methods such as thermal, wet co-spinning assembly, or electropolymerization have been used separately or collectively to coat the graphene-based materials on felt cathodes. For instance, electropolymerization has been well received for its simple operation, high polymerization rates, and capability to combine the advantages of multiple materials [63]. Liu, et al. [64] applied electropolymerization to obtain the GO/PEDOT:NaPSS-GF and achieved much lower Ec and higher current responses, coulomb efficiency, and H_2O_2 productivity for its high selectivity toward 2-electron ORR, and finally significantly improved TOC and COD removal efficiencies [64]. For gaining homogeneous film on felt electrodes from suspensions containing well-dispersed charged particles like graphene oxide (GO) solutions, electrodeposition showed excellent properties, e.g., easy scalability, simple operation, high deposition rates, and no need for binders [65]. Asgari, et al. [66] deposited the N-rGO on the CF by the electrochemical reduction. The N-rGO/CF showed a larger BET specific surface area, a higher response current, an improved oxygen reduction activity, and a higher H_2O_2 generation rate compared with the bare CF. Under the optimal condition, the N-rGO/CF cathode decreased the electrical Ec and increased the diuron degradation rate compared with the raw CF cathode. No obvious difference in the H_2O_2 generation after 10 cycle tests and the increased BOD_5/COD ratio from 0.041 to 0.4 confirmed the admirable stability of the

N-rGO/CF and the significantly improved biodegradability of the pesticide wastewater [66].

3.5 Carbon nanotubes-based modification

Carbon nanotubes (CNTs) have been competitive for the modification of felt cathodes owing to their thermal and electrical conductivities, significantly large surface areas, and mechanical flexibility [67]. The immobilization of CNTs on the surface of felt materials or onto the supporting membrane depends on the use of PTFE. As a type of binder, PTFE has dual roles: imparting some hydrophobic character to the cathode materials and pasting the high surface modified CNTs into the cohesive layer [68]. When applying these successfully modified cathodes in the EF process without additional catalysts, it has been found that the degradation rates of POPs were increased while the toxicities of wastewater were decreased. A remarkable improvement in the degradation efficiency of cefazolin (89.9%) was found within 100 min [68], while 90.2% removal of atrazine remained even after 8 cycle tests under the near-neutral pH condition using the bifunctional composite cathode co-modified with CNTs and N-doped carbon CoFe alloy [69]. Besides, CNTs could be combined with some materials that offer more active sites for improving the ORR. For instance, Li, et al. [70] coated the mixture of CNTs and g-C_3N_4 on the surface of CF and observed 86.0% removal of fulvic acids with the H_2O_2 production rate of 3.96 $mg \cdot h^{-1} \cdot cm^{-2}$. The GDEs were fabricated mainly from F-CNT, and results showed that much higher CE (89.5%) and H_2O_2 production (47.6 $mg \cdot L^{-1}$) than those of CNT modified GDEs (70.1%

and 29.6 mg·L^{-1}). Moreover, the high catalytic activities of these modified cathodes based on CNTs persisted after several consecutive cycle tests [71, 72].

It needs to be highlighted that in the absence of binders, the modified cathode could be obtained by loading the acidified CNTs on the graphite plate through the grind operation. After the modification, the cathode could exhibit a high activity towards the electro-reduction of Fe^{3+} to Fe^{2+} and help the EF process achieve higher and faster degradation of *p*-NP [73]. Also, the CNT cavities could provide an isolated environment for iron to obtain low iron leaching. The valences and positions of iron on CNTs could effectively improve the H_2O_2 yield to enhance the HEF activity and reduce the iron leaching to enforce the reusability of cathodes. The cathode confined iron in the interior of CNTs cavities also produced a faster phenol removal rate (9.68 times faster) compared with those confined iron on the walls of CNTs. And it's Fe^0 rather than iron oxide beneficial for H_2O_2 selectivity through the 2-electron ORR process (2.43 times higher) and the phenol removal rate (21.44 times faster) [74-77].

3.6 Polymer-based modification

Polypyrrole (PPy) and polyaniline (PANi) are the most common conducting polymers for cathode materials modification for their environmental stability, high electrical conductivity, and ease of preparation [78, 79]. The coating of conductive polymer film on the surface of the cathode is often carried out by the electropolymerization process in the solution containing monomers. However, the electropolymerized materials have

distinctive properties that aren't peculiar to the corresponding monomers [80, 81]. As described in **Fig. 3a**, a composite cathode of PANi modified GF (PANi/6-GF) synthesized by electrodeposition was proposed and utilized in the electrochemical advanced oxidation process system to degrade POPs. The results showed that the electron transfer of GF and graphitic N and pyridinic N in PANI/6-GF increased not only the electrocatalytic activity but the selectivity for the 2-electron ORR activity concerning the H_2O_2 production. Thus, the degradation rates of bisphenol A have been remarkably enhanced compared with the bare GF even after 10 cycle tests [82]. As seen in **Fig. 3b**, a novel binder-free anthraquinone (AQS)/PANi modified CF cathode electrode for selective H_2O_2 production and efficient contaminant removal in EF was also fabricated by the cyclic voltammetric electrodeposition method. Besides 98.8% RhB removal within 60 min, $O_2^{\bullet-}$ and $OH^{\bullet}$ were found as the main reactive radical species that conspicuously influenced the pollutant removal performance [83]. As shown in **Fig. 3c**, PPy and AQS were prepared and investigated in the modification of porous CF. With the approximately 2.5 times higher specific surface area than that of the pristine CF by BET and the decrease in the charge transfer resistance from 35,250 to 2.24 Ω by electrochemical impedance spectroscopy (EIS), the modified cathode for an efficient EF process ensured more active sites available and a faster mass transfer efficiency for ORR. Thus, almost 100.0% of RhB was destructed within 1 h, and the degradation efficiency of RhB in the EF system with the modified cathode remained higher than 99.0% after 5 cycle tests [84].

In addition, the metal-organic framework (MOF), known as a coordination polymer and well-ordered structure materials with organic blocks and metal centers, could be a reliable template for the fabrication of functional carbonous cathode materials [85]. The MOF-derived porous carbon had excellent performance in ORR because of its high surface area, tunable functionalities, and uniform heteroatom (N, F, S, P, B) doping, which could offer more active sites and shorten the diffusion length [86]. Zeolitic imidazolate framework-8 (ZIF-8), one of the representative MOFs that is inexpensive and contains 24.7 wt% nitrogen [87], was employed as the precursor to modify CF. Some OGs and nanoparticles grew on the ZIF-8/Actived CF (ACF) cathode surface, which remarkably improved the electrochemical performance and the hydrophilic property. Higher H_2O_2 production and CE of 1,545.1 $mg \cdot L^{-1}$ and 98.8%, respectively, with low electric Ec (<35.0 $kWh \cdot kg^{-1}$) and the complete TC removal within 20 min proposed this improved EF system with an efficient cathode to be a good alternative process for the removal of contaminants [88]. In the application of the MOF-derived materials in the EF system, the porous carbon-loaded metal oxides had excellent performance because of the carbon as the adsorption site with the metal oxides activating H_2O_2, thus enhancing the removal of pollutants [89]. A novel controlled pyrolysis method was applied to fabricate the quasi-MOF derivative-based cathode by pyrolyzing MIL-101(Fe) coated on the polyaniline-modified CF paper at 400 °C. The results showed that 100.0% of *p*-NP and 52.0% of TOC were removed in 2 h, indicating that the modified electrode had less Ec and more efficient mineralization CE compared with unmodified electrodes [90]. Also, a number of

Mn/Co MOFs derivatives modified GF (Mn_xCo_{3-x}@C-GF) were made without the use of any binder, which was applied to the removal of ciprofloxacin (CIP). By adjusting the proportion of Mn/Co in the MOF-74 precursor, the cathode presented excellent catalytic ability with faster electron transfer and hierarchical porous structure. In 60 min, the CIP degradation efficiency reached 99.8% and kept good stability during 4 cycle tests [9]. Zhou, et al. [91] successfully fabricated Mn/Fe@porous carbon through simple carbonization of Mn-doped MIL-53(Fe) precursor and applied it as cathode modification in $^{\bullet}OH$ based EF process for the degradation of triclosan (TCS). In addition to great stability, a low Ec, a high electrocatalytic activity, and a high degradation efficiency for TCS degradation over a wide range of pH, a possible TCS degradation pathway that proved the toxicity reduction of TCS by the EF process was deduced [91].

3.7 Cathode modification based on other materials

Carbon nanofibers (CNFs) appear to be an ideal candidate to modify the cathode materials in the EF system, considering their unique mechanical, electrical, and physicochemical properties [92, 93]. Li, et al. [94] applied the Fe/Co/Zn-tri-metal co-doped carbon nanofibers (Fe/Co/Zn@C-NCNFs-800) to modify the cathode by carbonizing the electrospun Fe-Co-Zn-ZIF@PAN for the enrofloxacin (ENR) degradation in the EF system. The higher specific surface area of the modified cathode increased the exposure of catalytic active sites which was instrumental in H_2O_2 activation. Therefore, it was found that the cathode with greater catalytic

activity, higher corrosison potential , and smaller electrochemical impedance compared to the Fe-Co-Zn-ZIF@PAN precursor resulted in an extraordinary ENR degradation efficiency, a fast generation rate and high remarkable yield of H_2O_2, and a relatively low Ec.

From the environmental perspective, it's worth noticing that agro-industrial waste has the great potential to fabricate carbonaceous electrodes for the EF technology [95, 96]. The modified cathode was prepared by carbon paste made from the uniform mixing of different percentages of graphite, agro-industrial residue activated carbon (orange peel activated carbon, or spent coffee ground activated carbon (SAC)), and silicone oil used as the binder. The results showed that the cathode modified with SAC had a larger efficiency (reaching 99.0% discoloration within 2 h), illustrating its possibility to turn waste into treasure [97].

4 Discussion and Perspectives

EF, one of the most promising AOPs, has exhibited great success in the degradation of various contaminants present in wastewater. In the EF process, H_2O_2 is electro-generated *in situ* via the preferable 2-electron ORR on the cathode with the participation of catalysts mainly including solid catalysts and Fe^{2+}. Fe^{2+} has been preferably used considering its higher activity and longer service life than solid catalysts such as natural FeS_2 [5]. It needs to be highlighted that the catalyst concentration plays a vital role in the EF process. Generally, the increase in the

catalyst concentration triggers higher •OH production and thus higher degradation of POPs [33]. However, an excessive Fe^{2+} concentration (i.e., higher than the optimum value) might lead to unsatisfying degradation performance due to the faster conversion of Fe^{2+} to Fe^{3+} which might deplete •OH through **Eq. 10** [98]. To overcome the limitations of catalyst application, increase the utilization and stability of EF in a wider pH range, improve the degradation efficiency of POPs with a lower Ec, and minimize the subsequent treatment of iron sludge, the applied cathodes fabricated by different modification methods have become the mainstream of research in this field of EF. This review summarized widely used approaches to modify cathodes including thermal, (electro) chemical, metallic, graphene-based, CNTs-based, and polymer-based treatments. Some specific methods for preparing the desired cathodes were described, together with their reported extraordinary performances in the removal of POPs.

$$\bullet OH + Fe^{2+} + H^{+} \rightarrow Fe^{3+} + H_2O \quad (10)$$

Generally speaking, the thermal treatment is a simple way to modify cathodes [23]. Though thermal activation can retain the structural integrity of GF by selectively etching the amorphous carbon and obtain good stability by generating stable reactive sites [99], the thermal treatment usually demands a high temperature, leading to high associated costs [26, 100]. Comparatively, the chemical treatment is a simple method that doesn't require a high temperature and is able to induce special structures such as

the stable three-phase interface to retain the stability [43]. It not only makes the modified process more economical and safer but combines the virtues of thermal activation and oxidant oxidation [40, 42, 101]. However, controlling the degree of oxidation remains a difficulty due to the diverse operating conditions involved (e.g., temperature, reaction time, oxidant type, and reagent concentration) [45, 53]. The electrochemical treatment can be conducted in a controlled manner by the easily adjustable treatment current and time [50]. Moreover, it can introduce some OGs that would barely change after cycle tests on the surface of the cathodes to improve their reusability [49]. However, this approach tends to consume a significant amount of energy and is limited in practical applications [40]. Nowadays, the metal modified cathode electrodes become popular since they can overcome the drawbacks of the traditional EF process, e.g., the attainment of the highest removal efficiency at a pH of around 3, the necessity of subsequent treatment of iron sludge, and the accompanying corrosion of structures in the acidic environment [7, 8]. Some metal modified cathodes were reported to maintain good reusability due to the structural presence of heterogeneous catalysts, for instance, layered double hydroxide particles, the well-confined nanoparticles of transition metal [7, 59]. However, the leaching of some precursor metallic materials from the metal modified cathodes that are considered more toxic than the targeted pollutants may incur more serious environmental problems [102]. In the graphene-based modification, GO and rGo can serve as ideal candidates to produce more $^{\bullet}OH$ owing to their superior conductivity [103, 104]. Also, they are even in favor of the Fe^{2+} regeneration from Fe^{3+} (i.e., **Eq. 3**) in solutions and

therefore enhance the stability of the EF system [105]. The CNTs-based modification is preferred by some researchers in the EF system. CNTs can boost the redox cycles of Fe between different valence states (i.e., **Eq. 3**) for their favorable electron migration properties and unique electronic structure [106, 107]. It can also provide an isolated environment for iron to achieve high efficiency with low iron leaching [74]. Despite all this, both of these two modification methods are usually supported on a carbon carrier by complicated steps [9]. Also, with the participation of the binder in the modification, the cathodic conductivities may be reduced and the reactant accesses to the reactive sites on the surface of the cathodes are likely to be hindered in some cases [30]. The polymer-based modification gets its place for equipping the cathodes with good conductivity and high chemical stability that are instrumental in pursuing high pollutant degradation efficacy and reusability of the EF system. Thus, this modification method has room for improvement considering its stringent modified conditions which would increase the costs and complexity of material preparation [9].

Given the aforementioned pros and cons, it's hard to conclude the best modification method. The decision regarding the most suitable method should be made based on the idiographic application environments and the purpose of fabricated cathodes. In this sense, this review would provide both easy access and state-of-the-art research for those who are in need of or interested in viable methods for modifying the cathode in EF.

All in all, continuous research input on cathode modification is needed, which hopefully would lead to the identification of methods to enable large-scale applications of EF. To this end, there could be two main directions driving future research in the relevant field. The first can come from seeking new materials with unique characteristics (i.e., high stability, non-toxicity, and catalytic ability) to modify pristine felts. For example, graphene could be deposited with conductive polymers or metallic particles to overcome the shortcomings of the traditional EF including the use of binder and the leaching of metallic materials. The other is the upgrade of current modification methods. In the electrocatalytic degradation process, a series of transition metal encapsulated nitrogen-doped CNTs (M@N-C, M=Cu, Fe, Ni, Co, etc.) as bifunctional cathodes have been proposed to achieve high selectivity for H_2O_2 and efficient degradation of pollutants. For example, in the self-sufficient electrocatalytic degradation, the Co@N-C cathode displayed the highest activity that enabled about 100% SMZ removal at pH ≤ 7 compared with Cu@N-C, Ni@N-C, Fe@N-C cathode [108]. However, the potential of applying these bifunctional cathodes in the EF process to the degradation of POPs still needs to be evaluated considering the high costs and long time associated with the complicated fabrication process. Moreover, some novel dual cathodes modified by different aforementioned methods could be placed in the same system to reduce the costs and enhance the performance of the EF system. For instance, for the higher production of H_2O_2 and $^{\bullet}OH$, two cathodes modified by the chemical and metallic treatments were coupled in the EF system and attained 96.0% TC degradation [58]. On one hand, the dual cathodes would gather

together multiple advantages such as more H_2O_2 production and high chemical stability and reusability. On the other hand, the use of dual cathodes would avoid the difficulty of implementing two effective modification methods on a single cathode.

When evaluating the performance of the modified cathodes in the EF system, attention should be given to the degradability and toxicity of intermediates as well as the final products of the targeted POPs. In fact, some intermediates can show lower degradability and even higher toxicity than those of undegraded POPs such as 4-chlorophenol, ranitidine, and sulfadiazine [109-111]. When combining the EF process with modified cathodes and other processes in real applications, the complexity and interaction of multiple contaminants present in the wastewater need to be considered, in addition to the conventional pollutants present in wastewater (e.g., organic COD and ammonium). For instance, CIP, LEV, OTC, and SMZ can all be found in pharmaceutical wastewater [40, 42, 112-114]. In this case, a novel modified cathode that works for the simultaneous removal of these different POPs should be fabricated.

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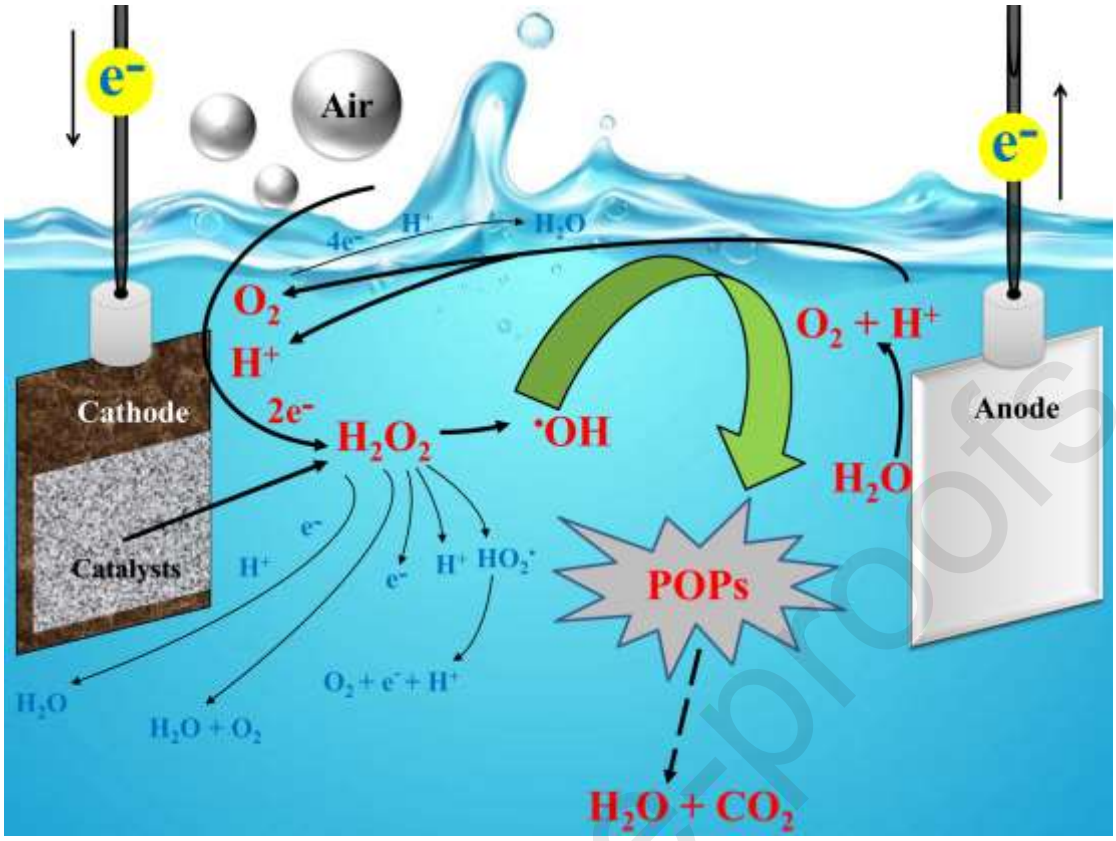

Fig. 1. Basic mechanisms of the EF process.

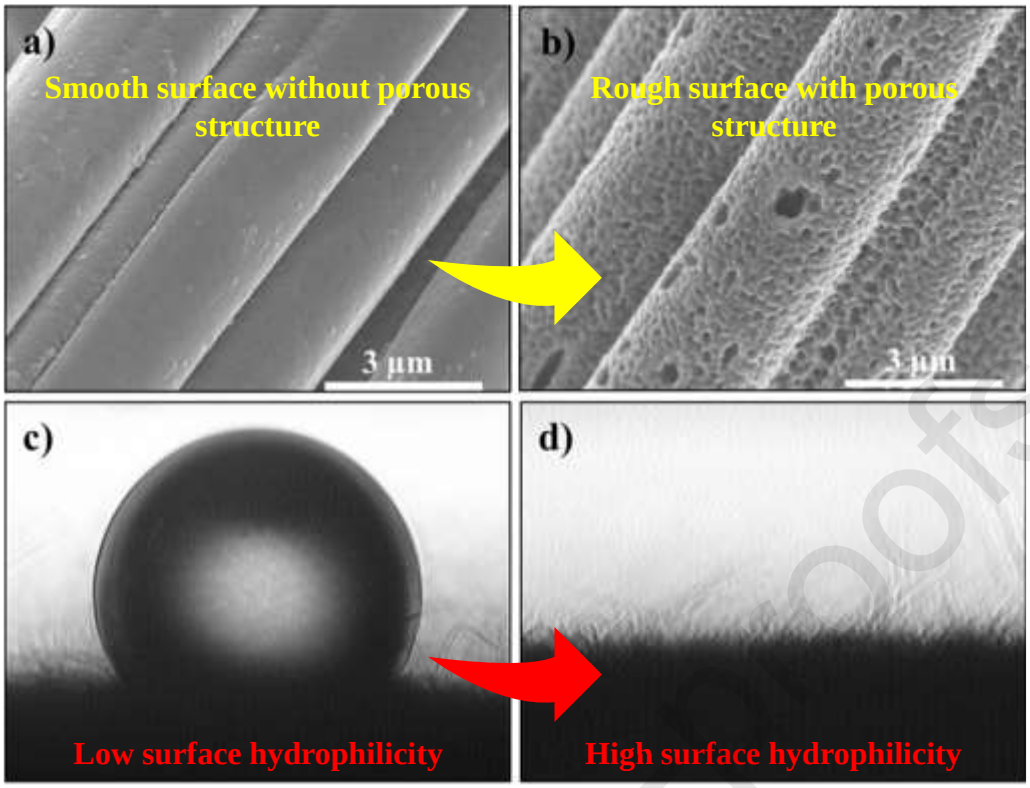

Fig. 2. Properties of raw carbon felt (raw CF) and porous carbon felt (PCF) after thermal treatment at 1000 °C for 1 h under nitrogen flow mixed with 1% oxygen: SEM images of (a) raw CF and (b) PCF, shapes of water droplets formed on (c) raw CF and (d) PCF. Reproduced from Ref. [26] with permission from Elsevier.

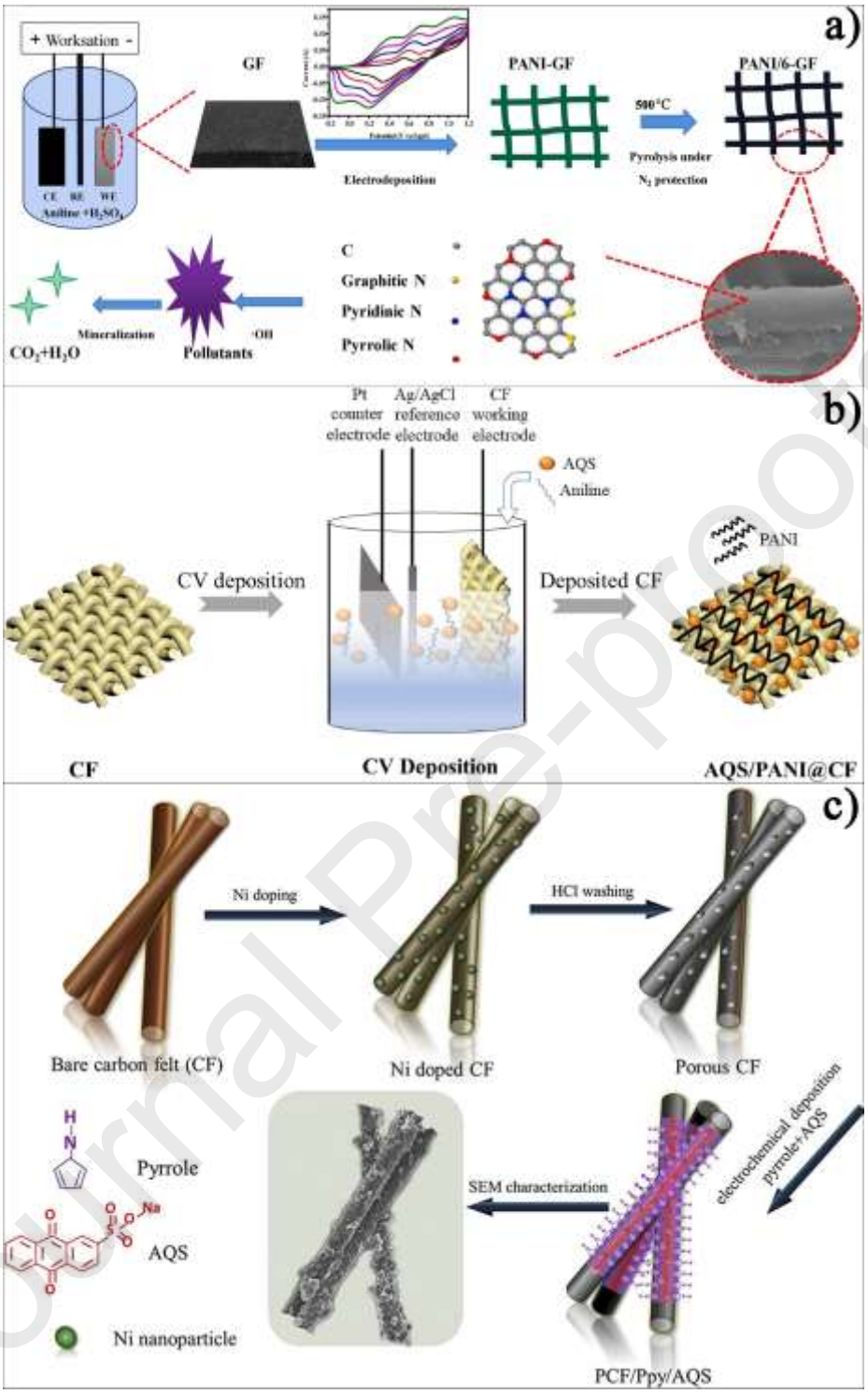

Fig. 3. Flow chart of preparing (a) polyaniline-derived carbon nanofiber modified electrode *in situ* without binder; (b) anthraquinone/polyaniline@carbon felt cathode; (c) porous carbon felt cathode modified by polypyrrole and anthraquinone 2-sulfonate. Reproduced from Refs. [82-84] with permission from Elsevier.

Table 1. Literature reported EF processes with cathodes modified by the metallic treatment to remove targeted pollutants.

Cathode	Anode	Model pollutant	Current/Voltage	Air/O_2 flow rate	Pollutant concentration	Optimum pH	Temperature	Time	Current efficiency/Specific energy consumption	H_2O_2 yield	Removal efficiency	Ref.
Fe/AC/Ni	DSA	Coking wastewater	10 V	-	2970.24 mg·L^{-1} of COD and 80.4 mg·L^{-1} of NH_3-N	3.88	-	420 min	-	-	88.91-96.65% of COD and 100.0% of NH_3-N	[114]
TFD@CF	Pt sheet	Methyl orange	10 mA·cm^{-2}	0.5 L·min^{-1} of O_2 flow rate	50 mg·L^{-1}	Applicable in a wide pH range	-	50 min	2.98 kW h·kg^{-1}·COD^{-1}	> 100 ppm	95.4%	[115]
$Cu_{0.33}Fe_{0.67}$NBDC-300/GF	BDD	Sulfamethoxazole	7.5 mA·cm^{-2}	0.6 L·min^{-1} of aeration rate	10 mg·L^{-1}	4.0/5.6	Room temperature (25±1 ℃)	30 min/45 min	-	-	100.0%	[112]
$CoFe_2O_4$/CF	Pt/Ti plate	Tartrazine	8.33 mA cm^{-2}	50 mL·min^{-1} of air flow rate	50 mg·L^{-1}	3.0	Room temperature (about 25 ℃)	40min	6.88 kWh·kg^{-1}·COD^{-1}	Without accumulation in the solution	97.05% of decolorization and 22.51% of TOC	[116]
$Fe^{II}Fe^{III}$ LDH/CF	Ti/RuO_2- IrO_2	Ciprofloxacin	200 mA	-	0.2 mM	Remained stable over a wide pH range	-	Within 90 min	-	-	88.11%	[117]
ACF and FeOCl/CC	Carbon plate	Antibiotic wastewater	-0.6 V vs Ag/AgCl	4 mL·min^{-1} of O_2 flow rate	10 mg·L^{-1}	5.0	-	-	45 kWh·kg^{-1}·TOC^{-1}	3.4 mM in 60 min	95.0% of degradation with 1.5 h and 88.0% of mineralization within 4 h	[58]
Ce/Fe@NPC-GF	Pt foil	Sulfamethoxazole	20 mA	350 mL·min^{-1} of extra aeration rate	20 mg·L^{-1}	3.0	-	120 min	1.44 kWh·m^{-3}	4.47 mg·L^{-1}	Basically degraded	[118]
Fe@Co/GF	Anode biofilm	Phenolic compounds	-	500 mL·min^{-1} of air flow rate	20 mg·L^{-1}	3.0	30 ℃	Within 22 h	-	152.40 μM	100.0% of vanillic acid, 94.32% of syringic acid and 100.0% of 4-hydroxybenzoic acid	[119]
FMBO-GF	Ti/RuO_2- IrO_2	Ciprofloxacin	2 mA·cm^{-2}	-	25 mg·L^{-1}	Over a wide pH range	Room temperature (25 ℃)	-	20.26% of MCE	-	92.89% of CIP in 30 min and 93.77% of TOC in 2 h	[113]
MNP-AC	Graphite	Phenazopyridine	0.2 A	-	30 mg·L^{-1}	3.0	Room temperature (25 ℃)	120 min	-	1669 μM	98.21%	[120]
CFP@MnO_2-Fe_3O_4/C	BDD	Shale gas fracturing flowback wastewater	5 mA·cm^{-2}	300 mL·min^{-1} of air flow rate	50 mg·L^{-1} model pollutants or 100 mL real fracturing flowback wastewater	3.0	25 ℃	4 h	6.9 kWh·kg^{-1}·COD^{-1}	175 mg·L^{-1} at 90 min	65.2% of TOC and 74.8% of COD	[59]
FeS_2/CF	DSA	Carbamazepine	1.875 mA·cm^{-2}	100 mL·min^{-1} of air flow rate	5 mg·L^{-1}, 0.02 mM	7.0	-	60 min	-	16.82 mg·L^{-1} after 60 min	81.54%	[121]
FeC@Co/N/CF	Bare CF	EDTA-Ni(II)	30 mA	-	10 M	3.0	Room temperature	120 min	2.23 kWh·m^{-3}	62.5 mg·L^{-1}	97.5% of EDTA-Ni and 94.3% of TOC	[122]
$Fe^{II}Fe^{III}$ LDH-CF	BDD	Pharmaceutical ofloxacin	9.37 mA·cm^{-2}	0.75 L·min^{-1} of aeration flow rate	0.1 mM	Even stable at neutral pH	Ambient temperature	8 h	2.05 kWh·g^{-1} ·TOC^{-1}	< 2.5 mg·L^{-1}	Complete TOC removal	[7]
Fe/AC/Ni	DSA	Landfill leachate nanofiltration concentrate	10 V	Provide the requisite O_2	2567.39 mg·L^{-1} of COD and 3276 mg·L^{-1} of NH_3-N	2.81/3.90	-	300 min	-	-	77.24 % of COD and 74.62 % of NH_3-N	[123]
MGF	Ti/RuO_2-IrO_2	Ciprofloxacin	400 mA	-	50 mg·L^{-1}	3.0	25±1 ℃	30 min/8 h	26.23% of MCE at 1 h and gradually decreased	-	95.62% of CIP and 94.0% of TOC	[124]
FeS_2/CF	BDD thin film deposited on a conductive Nb sheet	Anthracene	10 mA·cm^{-2}	-	5.62 μM	Applicable in a wide pH range	Room temperature (20 ℃)	20 min	-	-	> 80.0%	[57]

Table 2. Recently reported graphene-based cathode modifications in the EF process for the removal of various contaminants.

Cathode	Main raw materials of modification	Activation method	Anode	Contaminant	Removal efficiency/Performance improvement	Ref.
M-FeCoO/GO	$Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, GO solution, and urea	Thermal	Circular CF	Oxytetracycline	4.5 times higher electricity generation, 1.33 times higher OTC degradation and detoxification, 1.14 times higher H_2O_2 generation, and 2.63 times higher mineralization efficiency than CF	[125]
CF/GO/AQS	GO, AQS, PTFE, and ethanol	Thermal	Platinum	RhB	95.0% of RhB decolorization rate within 1 h (2.3 times higher than that of the unmodified cathode), -2.48 $mA \cdot cm^{-2}$ of the response current (about 6 times higher than that of the bare CF), 4.84 times higher H_2O_2 yield than that of pristine CF and 89.9% of TOC removal with the corresponding Ec of 4.23 $kWh \cdot kg^{-1}$	[104]
GO/PEDOT: NaPSS modified GF	$LiClO_4$ aqueous solution, EDOT, NaPSS, and GO	Electropolymerization	Platinum wire	MB	Much higher H_2O_2 productivity, current response, and coulomb efficiency, 97.9% MB decolorization after 30 min and 100.0% MB removal after 60 min	[64]
3D rGOSF	GO LC aqueous dispersion, ethanol, HI, acetic acid, PTCA, and PTCDA	Wet co-spinning assembly combined with secondary thermal or chemical reduction	Pt foil	Bisphenol A (BPA), SMZ, and RhB	6.25 $mg \cdot cm^{-2} \cdot h$ of the H_2O_2 generation rate in the first hour, ~98.0% BPA removal within 30 min, nearly 100.0% removal of SMX and RhB in 50 and 40 min	[126]
TRGO-1100-ABC	TRGO-1100, graphite powder, ethanol, and PTFE	Thermal	Iridium oxide (Ti/IrO_2) plate	TC	66.0% TC removal in 5 min, 20.4 ± 0.8 $mg \cdot cm^{-2} \cdot h$ of the H_2O_2 generation rate and 94 ± 2% of the current efficiency	[127]
P-rGO/CF	CB, heteroatom-doped graphene, PTFE, and ethanol	Thermal	Iron plate	Carbamazepine (CBZ)	Better performance in electric Ec, H_2O_2 yield (137.68 $mg \cdot L^{-1}$) and removal efficiency (almost 100.0% CBZ removal)	[103]
N-rGO/CF	GO powder and lithium perchlorate	Electrodeposition	Ti/PbO_2	Diuron	Higher response current and H_2O_2 production rate, improved oxygen reduction activity, larger BET specific surface area, and the BOD_5/COD increased from 0.041 to 0.4 after 90 min	[66]
RGO-modified GADC	High-purity flake graphite, ethanol, PTFE, and GO	Superficial deposition	Pt wire	Penicillin sodium	91.13% of TOC removal and 56.8% of MCE with the average H_2O_2 production of 187.5 ~ 243.7 $mg \cdot L^{-1} \cdot h^{-1} \cdot cm^{-2}$	[128]

HIGHLIGHTS

- Mechanisms of EF and fundamentals/necessity of cathode modification.
- Current cathode modification methods with reported performances in removing POPs.

- Pros/cons and perspectives of cathode modification for EF degradation of POPs.