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Invited Review

Review of electrochemical degradation of phenolic compounds

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Abstract: Phenolic compounds are widely present in domestic and industrial sewage and have serious environmental hazards. Electrochemical oxidation (EO) is one of the most promising methods for sewage degradation because of its high efficiency, environmental compatibility, and safety. In this work, we present an in-depth overview of the mechanism and factors affecting the degradation of phenolic compounds by EO. In particular, the effects of treatment of phenolic compounds with different anode materials are discussed in detail. The non-active anode shows higher degradation efficiency, less intermediate accumulation, and lower energy consumption than the active anode. EO combined with other treatment methods (biological, photo, and Fenton) presents advantages, such as low energy consumption and high degradation rate. Meanwhile, the remaining drawbacks of the EO process in the phenolic compound treatment system have been discussed. Furthermore, future research directions are put forward to improve the feasibility of the practical application of EO technology.

Keywords: electrochemical oxidation; phenolic compounds; degradation mechanism; anode material

1. Introduction

With the rapid development of industries, water pollution by toxic organic pollutants has become serious. Phenolic compounds, as toxic organic compounds, exist in almost all industrial wastewaters, such as those of the petrochemical, coke oven, textile, rubber, paper, glass, and paint industries [1–2]. These compounds pose severe harm to human health and the whole ecosystem due to their mutagenicity and carcinogenicity at low concentrations. The concentration of phenol at 2 mg·L^{-1} is toxic to aquatic organisms, whereas concentrations between 10–100 mg·L^{-1} lead to death within 96 h. The World Health Organization proposed the 0.001 mg·L^{-1} concentration threshold for phenol in drinking water. Table 1 provides the amounts of phenol present in several industries [3]. The concentration of most wastewaters exceeds the toxicity limit. Thus, the degradation of phenolic compounds from industrial wastewater before discharge is a critical and urgent topic that must be explored. Various treatment methods, including chemical (e.g., coagulation, precipitation, and oxidation–reduction), physical (e.g., centrifugal separation, sedimentation, and filtration), physical–chemical techniques (e.g., membrane filtration, extraction, ion exchange, and adsorption), and biological (e.g., anaerobic and aerobic process) have been used to degrade and mineralize phenolic compounds in wastewater [4]. These methods present several problems, such as coagulation, adsorption, chemical oxidation, and filtration, which commonly cause secondary toxic pollution during the treatment process. The biological method shows low efficiency for degrading biorefractory contaminants caused by these pollutants inhibiting the normal function of microbial populations.

The developed advanced oxidation processes (AOPs), including electrochemical oxidation (EO), Fenton oxidation, sonochemical oxidation, ozone oxidation, and photochemical oxidation, are effective means to remedy such problems [5]. EO, a technology that is efficient in the treatment of refractory organic pollutants, has been developed in recent years. This method is regarded as green treatment technology because it only consumes clean reagents, i.e., electrons.

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In addition, EO exhibits a good corrosion resistance. Thus, this method can be used to treat highly toxic and corrosive pollutants. Moreover, EO technology has a high reaction rate and selectivity for pollutant removal and can be automated [6–7]. Related researches mainly include anode modification (e.g., particle doping [8–9], element doping [10–11], surfactant modification [12–13], and substrate modification [14]), optimization of operating parameters (e.g., the initial concentration of organic matter, electrolyte type and concentration, current density, and solution pH [15–16]), and mechanism of degradation [17–18].

Table 1. Concentrations of phenolic compounds in various industrial wastewaters. Adapted from *J. Environ. Chem. Eng.*, 8, D.M. Naguib and N.M. Badawy, Phenol removal from wastewater using waste products, 103592, Copyright 2020, with permission from Elsevier

Industrial	Phenol concentration / $(mg \cdot L^{-1})$
Petrochemical	200–1220
Coke ovens	600–3900
Textile	100–150
Rubber	3–10
Paper	20–80
Glass	40–2564
Paint	1.1

This review presents the progress, advantages, and disadvantages of various anode materials in the electrochemical degradation of phenolic compounds. By comparing the degradation rate, energy consumption (EC), current efficiency (CE), and other parameters, we hope to provide useful information regarding material selection for EO application to degrade phenolic compounds. Meanwhile, we also systematically discussed the mechanism, impact factors, and the performance of other tandem technologies. In addition, the challenge and direction of future improvement are discussed to improve the economic and technical feasibility of the considered method.

2. EO mechanism

Pollutants are removed by two patterns in the EO process: direct and indirect oxidation. Fig. 1 shows the EO mechanism summarized from previous studies [19–21]. In direct oxidation, organic compounds are first adsorbed on the electrode surface and then destroyed directly by electrons. Therefore, this process is affected by the transport rate of organic compounds and the electrocatalytic activity of anode materials. By comparison, indirect oxidation degrades organic compounds based on strong oxidizing agents, such as hydroxyl radicals (•OH), OCl^-, $S_2O_8^{2-}$, H_2O_2, and O_3. These agents are produced by anode or cathode reactions or both. The process is affected by the nature of electrode material, electrolyte, and other experimental conditions; these factors also affect the mechanism of the EO process (direct, indirect, or both).

Direct EO occurs when the electrochemical system potential is lower than the potential of the oxygen evolution reaction (1.23 V vs. standard hydrogen electrode (SHE)). In this

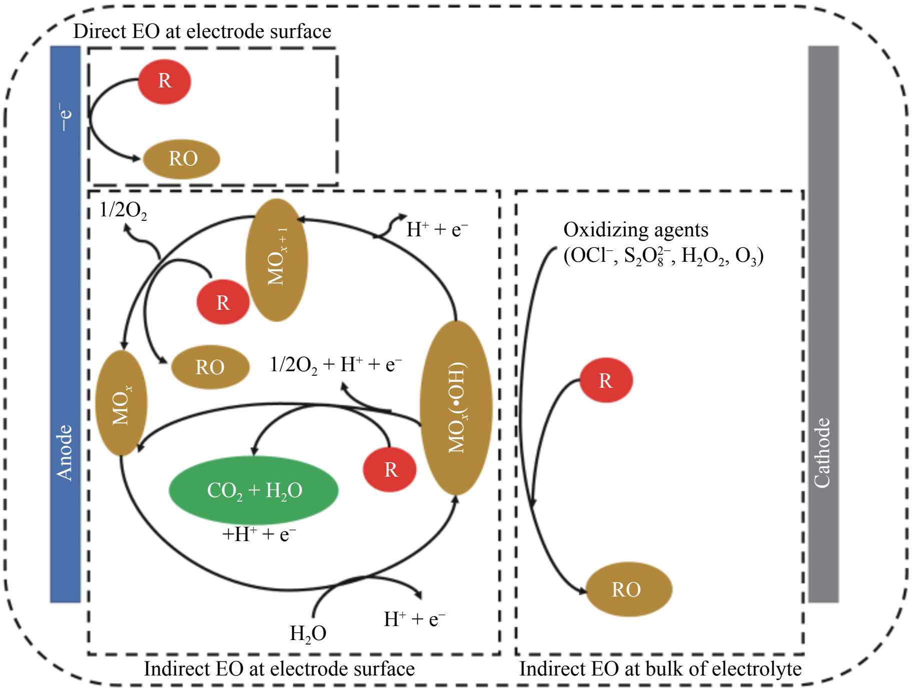


Fig. 1. Schematic of the EO mechanism for organic degradation [19–21] (RO—Oxidized organic pollutant; R—Targeted organic pollutant).

potential range, the current is used entirely to degrade organic pollutants, but a polymer film easily forms on the electrode surface [22]. In the presence of phenolic compounds or high concentration of pollutants, the surface pollution of the electrode is significant.

By contrast, indirect EO occurs in the higher-potential region where hydroxyl radicals (•OH) can be formed. •OH is effective for aromatic organic degradation, which is difficult to achieve by traditional methods. Other strong oxidizing substances generated from the bulk of the solution, such as •OH, OCl^-, $S_2O_8^{2-}$, H_2O_2, and O_3, can also oxidize organic pollutants, as shown in Eqs. (1)–(6).

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

$$2SO_4^{2-} + 2H^+ \rightarrow H_2S_2O_8 + 2e^- \quad (4)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (5)$$

$$O_2 + H_2O \rightarrow O_3 + 2e^- + 2H^+ \quad (6)$$

Based on the EO mechanism and pieces of literature about oxidation of phenolic compounds [23–25], we summarized the reasonable pathways for the degradation of phenolic compounds (Fig. 2). Here we used p-substituted phenols as model substrates. We not only provide the degradation pathways of direct and indirect EO by •OH (Fig. 2(a)) but also those of inorganic oxidants with •ClO as an example (Fig. 2(b)).

In Fig. 2(a), the first reaction pathway I represents the formation of polymeric products by attack either by benzoquinone or hydroquinone and then oxidation by •OH to CO_2 and H_2O (A → B → C/D → E → CO_2 + H_2O). The polymeric products are formed via C–C coupling or ether linkages and are more difficult to degrade than phenolics [26]. In parallel, the second reaction pathway II shows the •OH attack on benzoquinone or hydroquinone, causing benzene ring cleavage and production of C4 compounds. Then, the C4 compounds break down into smaller carboxylic acid molecules such as I/J and are eventually mineralized to CO_2 and H_2O (A → B → C/D → F/G → H → I → J → CO_2 + H_2O). Reaction pathways I and II occur simultaneously. If the benzene ring is cracked rapidly, the accumulated polymer

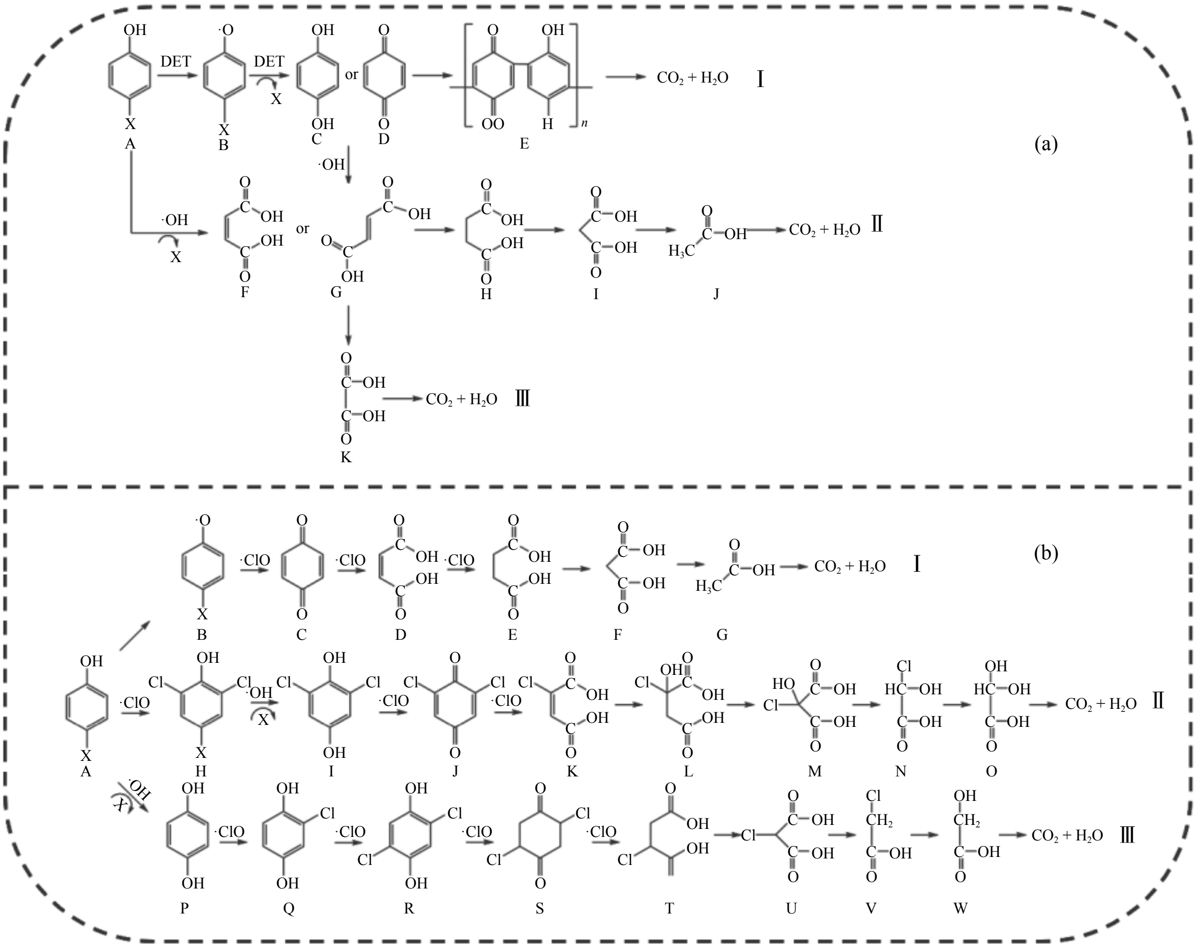


Fig. 2. Possible pathways for the degradation of phenolic compounds by EO: (a) oxidation by •OH (DET—Direct oxidation); (b) oxidation by •ClO [23–25].

will be small. The third reaction pathway III corresponds to the overall •OH induced reaction. The benzene ring is cracked by •OH attack to produce C2 compounds and is directly mineralized to CO_2 and H_2O.

Fig. 2(b) shows the oxidation process of phenolic compounds by •ClO. In pathway I, the phenolic compounds are first attacked by electrons and then oxidized by •ClO ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F \rightarrow G \rightarrow CO_2 + H_2O$). In pathway II, the phenolic compounds are first attacked by •ClO, whereas substituents X and Cl atoms are replaced by •OH and generate chloroquenone, which is easily oxidized by •ClO. As a result, the benzene ring is opened and mineralized into CO_2 and H_2O ($A \rightarrow H \rightarrow I \rightarrow J \rightarrow K \rightarrow L \rightarrow M \rightarrow N \rightarrow O \rightarrow CO_2 + H_2O$). In pathway III, phenolic compounds are first attacked by •OH, whereas substituent X is replaced by •OH and generates hydroquinone. Then, hydroquinone is oxidized by •ClO. The benzene ring is opened and finally transformed into CO_2 and H_2O ($A \rightarrow P \rightarrow Q \rightarrow R \rightarrow S \rightarrow T \rightarrow U \rightarrow V \rightarrow W \rightarrow CO_2 + H_2O$).

As shown in Fig. 2, the degradation pathways of phenolic compounds are complex. Although it has been widely studied, no consensus has been achieved regarding the EO degradation mechanism of phenolic compounds. Several studies [27] hold the view that organic compounds undergo indirect oxidation by •OH radicals, whereas direct EO plays no role in the oxidative degradation of organics. Direct and indirect EO are compared in the presence or absence of 0-nitrophenols (0-NPs) using the cyclic voltammetry curve (CV) test. Neither new oxidation nor reduction peak appears in the CV curve test with 0-NPs, which indicates that the 0-NPs are not directly but indirectly oxidized on the anodes. The detected concentration of •OH radicals and removal rate are identical to the conclusions of the CV test. The other standpoint is that organic pollutants are removed by direct EO on the anode surface [28]. Methanol and d3-methanol are adopted to competitively react with •OH, with the oxidation rate at proximity with that under different concentrations. This finding proves that organic degradation is not oxidized by •OH. Other studies [29] showed that the removal of organic matter is the cooperation result of direct and indirect oxidation. The different conclusions may be due to the influence of different electrode materials and electrolyte solution on the generation of oxidants.

3. Influencing factors of the EO process

The EO degradation of phenolic compounds is affected by various factors, such as substituents, electrode, current density, pH, electrolytes, initial organic concentration, and reactor. In addition, other minor influencing factors include the inter-electrode gap, temperature, cathode material, flow velocity, etc. In this section, we will describe several of the factors in detail.

3.1. Substituents

The different substitution groups ($-Cl$, $-CHO$, $-NO_2$, $-OCH_3$, etc.) and positions (ortho-, meta-, and para-) affect the degradation of organic pollutants. Therefore, we use para-phenol as target pollutant to research the effects of substituents on the treatment of phenolic compounds. The different substituents affect reactivity due to their capabilities to attract or push electron clouds. Based on this property, phenolic compounds are classified into electron-withdrawing and electron-donating groups. We summarize the structure and electrostatic potential distribution of several phenolic compounds in Table 2 [30–31].

The p-substituted electron-withdrawing groups have a higher degradation rate than electron-donating groups because the electro-withdrawing groups are easily released from the benzene ring [30–31]. In general, Hammett's constant (σ) is used to reflect the influence of structural moieties on electronic characteristics, and its positive and negative values correspond to the electron-withdrawing and electron-donating groups, respectively. Studies [32] described the electrochemical oxidative degradation process of p-phenol compounds through a pseudo-first-order kinetic model and revealed that the first-order constant (k_1) follows that of $p\text{-}NO_2 > p\text{-}Cl > p\text{-}CHO > Ph > p\text{-}OCH_3$ order. This result confirms that the degradation rate of electron-withdrawing groups is higher than that of electron-donating groups. Fig. 3 shows the degradation efficiency of phenolic compounds with different substituent groups and the relationship between k_1 and σ [30]. As shown in Fig. 3, the reaction rate of p-substituted phenolic rises with the increase of σ.

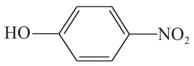
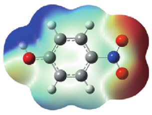
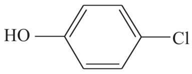
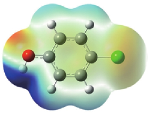
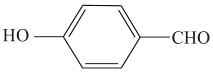
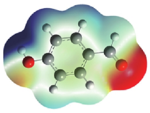
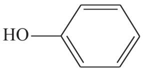
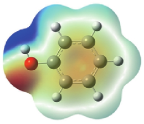
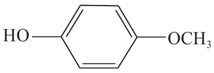
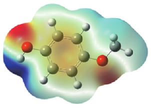
3.2. Current density

When working in the galvanostatic mode of EO technology, current density is an important parameter that determines the production of strong oxidizing substances. In general, the degradation rate of organic pollutants increases with the increase in current density because a high current density can promote the formation of strong oxidizing substances in a given time. Fig. 4 shows the effects of current density on the EO process [33]. The test conditions are as follows: the initial concentration of phenol is 50 $mg \cdot dm^3$, and the electrolyte is 10 mM $NaNO_2$. As the current density increases, the degradation rate and total organic carbon (TOC) removal rate increase [33]. However, given secondary reactions, such as oxygen evolution and polarization, the value of current density cannot be increased indefinitely. Furthermore, a large current density will result in a low CE. Thus, an optimal current density must be selected by combining the degradation of pollutants and CE. At present, most researchers pursue high degradation rate at the expense of low CE.

3.3. Anode

The anode material plays a vital role in the EO process. It

Table 2. Structure and several properties of phenolic compounds [30–31]. The figures in the table are reprinted from *Chemosphere*, 248, H. Jiang, C.Y. Dang, W. Liu, T. Wang, Radical attack and mineralization mechanisms on electrochemical oxidation of p-substituted phenols at boron-doped diamond anodes, 126033, Copyright 2020, with permission from Elsevier

Phenolics	Abbreviation	Chemical structure	Electrostatic potential distribution*	Electron-donating or electron-withdrawing
p-nitrophenol	p-NO_2			Electron-withdrawing
p-chlorophenol	p-Cl			Electron-withdrawing
p-hydroxybenzaldehyde	p-CHO			Electron-withdrawing
Phenol	Ph			Electron-donating
p-methoxyphenol	p-OCH_3			Electron-donating

Note: * -4×10^{-2}  4×10^{-2} The red and blue colors represent the most negative (electron-rich) and positive potential (electron-deficient) regions.

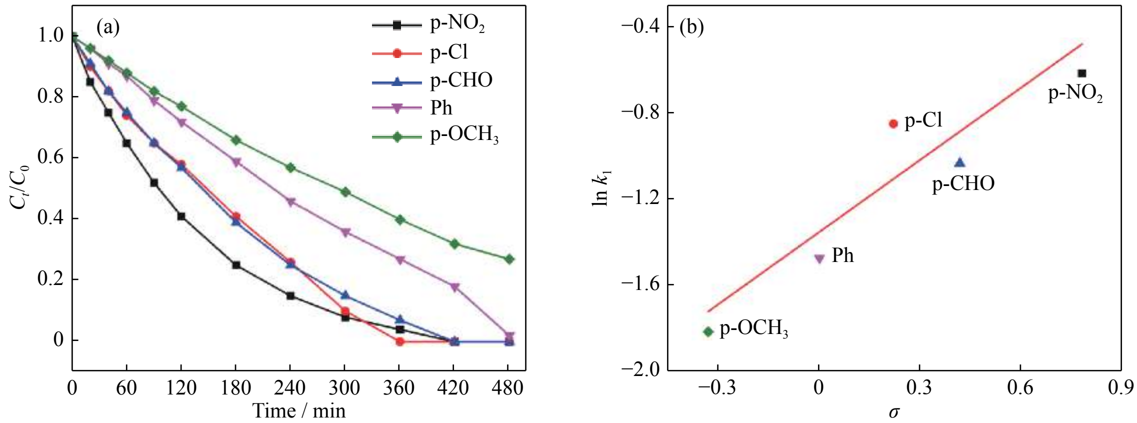


Fig. 3. (a) EO degradation of phenolic compounds (C_0—Initial concentration; C_t—Concentration at time t); (b) relationship between the reaction rate constant and Hammett's constant. Adapted from *Chemosphere*, 248, H. Jiang, C.Y. Dang, W. Liu, T. Wang, Radical attack and mineralization mechanisms on electrochemical oxidation of p-substituted phenols at boron-doped diamond anodes, 126033, Copyright 2020, with permission from Elsevier.

affects the efficiency of electrochemical treatment processes, the type of oxidation mechanism, and the formation of by-products. In general, anode materials mainly consist of three types, namely, metal electrodes that primarily include platinum, titanium, and stainless steel; carbon electrodes that comprise boron-doped diamond (BDD), graphite electrode, and activated carbon fiber; metal oxide electrodes that consist of lead dioxide, stannic oxide, and iridium oxide. These types of electrodes will be described in detail as follows.

3.3.1. Platinum electrode

The metal electrode is bare and has no oxide film on its surface. Although metal electrodes have good conductivity, as an anode, they may be dissolved in the electrolytic process, resulting in anode loss. In addition, the mixing of metal ions into the solution can form secondary pollution. The metal electrodes commonly used in electrochemical wastewater treatment are inert metals (platinum) due to their strong corrosion resistance, relative low oxygen evolution potential (1.6

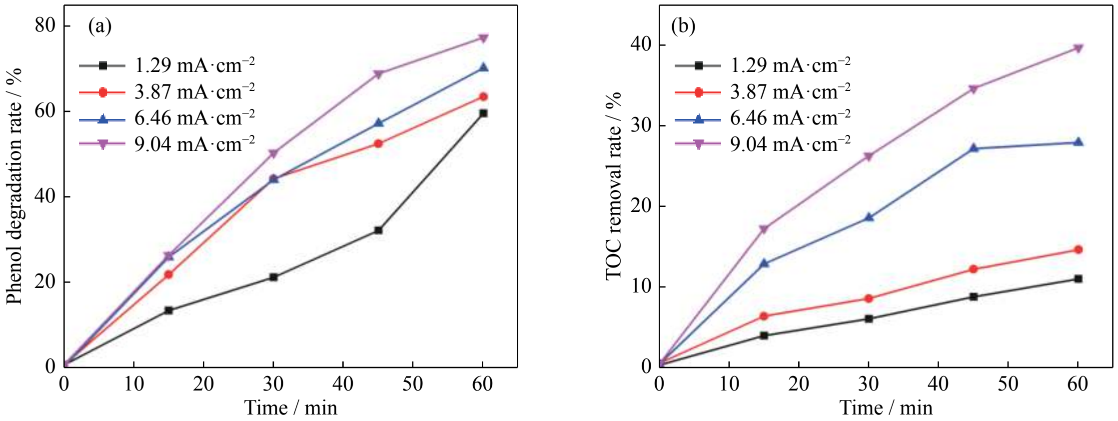


Fig. 4. Effects of current density on the EO process: (a) phenol degradation rate; (b) TOC removal rate. Adapted from *J. Hazard. Mater.*, 373, C.Y. Zhang, J.Y. Dong, M. Liu, W.J. Zhao, and D.G. Fu, The role of nitrite in electrocatalytic oxidation of phenol: An unexpected nitration process relevant to groundwater remediation with boron-doped diamond electrode, 547-557, Copyright 2019, with permission from Elsevier.

V vs. SHE, 0.5 M H_2SO_4), and high electrocatalytic activity. Considering that Pt is a precious metal, Ti is usually adopted as the substrate when coating a thin layer of Pt to reduce cost. Zambrano and Min [34] carried out the oxidation of phenol using Ti/Pt as an anode electrode. The degradation rate of phenol reaches 93% after 120 min.

3.3.2. Lead dioxide

PbO_2, an inexpensive material with good electrochemical stability and relatively high oxygen evolution potential, is commonly used as an anode material to degrade phenolic compounds by EO. PbO_2 electrode uses β-PbO_2 deposited on a Ti substrate as the anode activity layer by electrodeposition. However, the application of PbO_2 electrodes faces the problem of flaking of PbO_2 coating from the Ti substrate, which reduces the service life of PbO_2 electrodes [35].

Several studies carried out modification experiments to improve the service life of PbO_2 electrode. The results showed that the incorporation of certain foreign ions cannot only enhance the stability of the PbO_2 electrode but also improve its electrocatalytic activity. Such foreign ions include Bi, F, Cu, Fe, nano-diamond, TiO_2, SnO_2, Co_3O_4, TiN, and rare earth compounds (such as Er_2O_3, Gd_2O_3, La_2O_3, ZrO_2, CeO_2, etc.) [10,36–39]. Other studies added a new layer, such as that made of nanoTiO_2, carbon nanotube (CNT), TiO_2 nanotube array, etc., to optimize the structure of the PbO_2 electrode [40–41]. Moreover, other research adopted foreign ions and added a new layer to improve the electrode performance [42]. Fig. 5 shows the effects of the modification of PbO_2 anode [10,36,39–42]. Modification can improve the densification of crystal structure, enhance the electrode stability, and boost the degradation rate of phenolic compounds. The reasons for the enhanced electrode stability and increment in electrocatalytic activity are as follows. First, the compact crystal structure can mask the electrolyte and active oxidative species penetration into the PbO_2 layer, thereby improving the service life of the PbO_2 electrode. Second, oxygen precipitation on the anode is one of the main reasons for the dissolution and peeling of the PbO_2 film. Therefore, the modified PbO_2 anode with a high oxygen evolution potential has a longer service life than pure PbO_2. Third, the modified electrode has a large surface area. Thus, its electrocatalytic activity and degradation rate are high.

3.3.3. BDD electrode

Carbon materials have long been used as electrodes because of their good electrical conductivity. Such materials mainly include graphene, ordered mesoporous carbon, carbon nanohorns, CNTs, carbon dots, and fullerene [43]. Carbon materials have been used for EO degradation of organic matter [44]. However, they have two disadvantages. First, when the reaction is accompanied by oxygen evolution, carbon reacts with oxygen to generate CO and CO_2, resulting in the corrosion of electrode materials. Second, carbon materials have low strength, and serious mechanical loss of electrodes occurs during operation. In recent years, the improvement of the mechanical strength and corrosion resistance of graphite materials has become an important research topic.

Different from other carbon materials, BDD has excellent mechanical strength and corrosion resistance. This material was first exploited in the late 1990s and has been used as an electrode material for wastewater treatment due to its strong EO capability, high oxygen evolution potential (2.3 V vs. SHE, 0.5 M H_2SO_4), and low background current [45]. In general, the BDD electrode prepared by chemical vapor deposition (CVD) includes two types: one is a thick free-standing film of BDD; the other type is thin-film BDD coated over a substrate, such as that made with Ti, Si, Ta, and Nb. Ti substrate stands out as a promising material due to its high corrosion resistance, excellent physical and mechanical properties, and good electrical conductivity. However, the main problem of the Ti/BDD electrode is its low service life. The adhesion and quality of BDD coating, the rough and porous structure of TiC, and the residual stress produced during CVD are

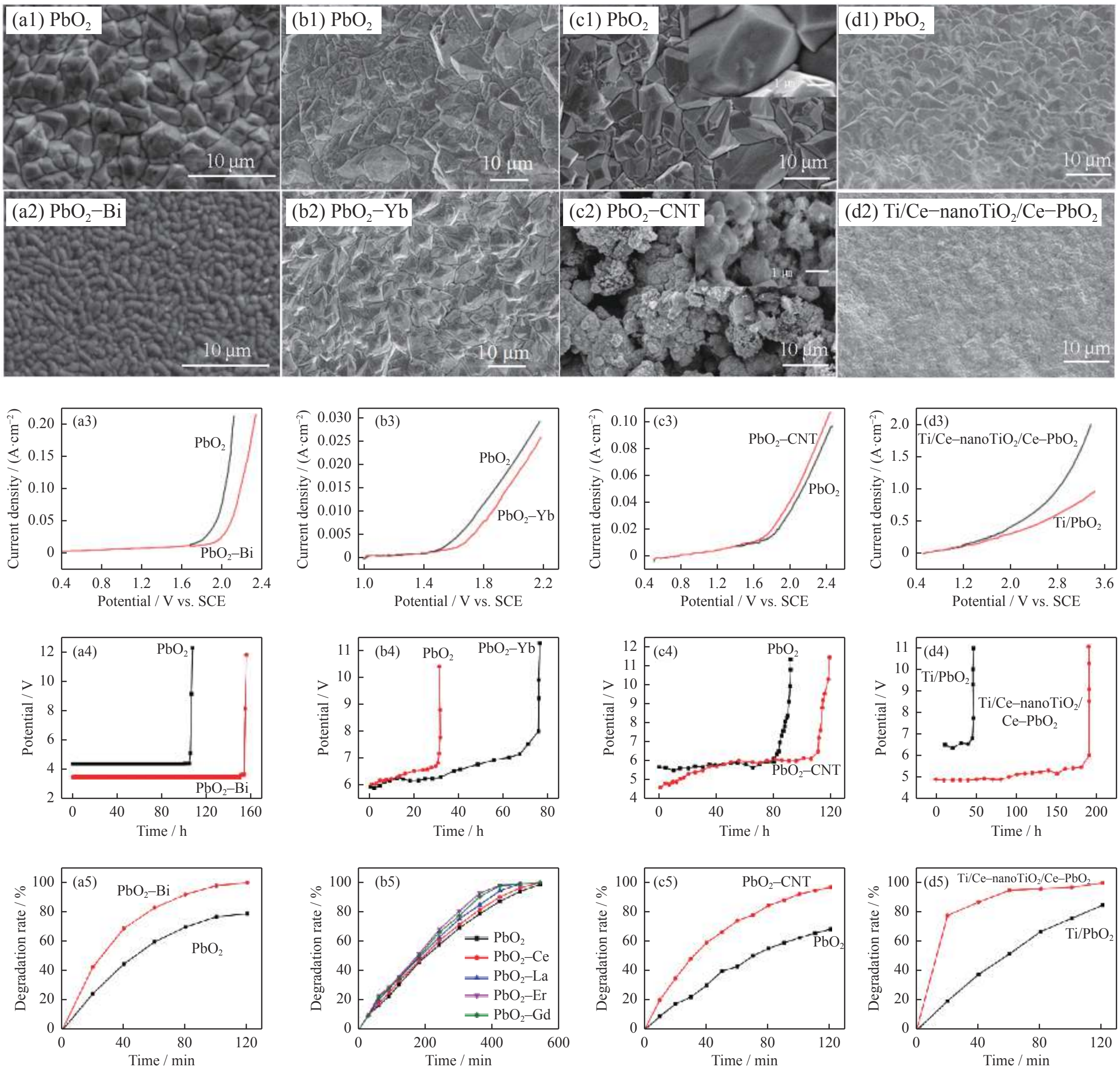


Fig. 5. Effects of modifying PbO_2 anodes: (a1, b1, c1, d1) scanning electron microscopy (SEM) images of pure PbO_2 anode; (a2, b2, c2, d2) SEM images of modified PbO_2 anode; (a3, b3, c3, d3) corresponding linear sweep voltammetry curves; (a4, b4, c4, d4) corresponding potential variation with time in accelerated life test; (a5, b5, c5, d5) corresponding degradation rates. (b1), (b2), (b3), and (b4) are adapted from *Sep. Purif. Technol.*, 211, Y.W. Yao, G.G. Teng, Y. Yang, C.J. Huang, B.C. Liu, and L. Guo, Electrochemical oxidation of acetamiprid using Yb-doped PbO_2 electrodes: Electrode characterization, influencing factors and degradation pathways, 456-466, Copyright 2019, with permission from Elsevier; (b5) is adapted from *Electrochim. Acta*, 53, J.T. Kong, S.Y. Shi, L.C. Kong, X.P. Zhu, and J.R. Ni, Preparation and characterization of PbO_2 electrodes doped with different rare earth oxides, 2048-2054, Copyright 2007, with permission from Elsevier; (c1), (c2), (c3), and (c4) are reprinted from *Electrochim. Acta*, 300, F. Xu, L.M. Chang, X.Y. Duan, W.H. Bai, X.Y. Sui, and X.S. Zhao, A novel layer-by-layer CNT/PbO_2 anode for high-efficiency removal of PCP-Na through combining adsorption/electrosorption and electrocatalysis, 53-66, Copyright 2019, with permission from Elsevier; (c5) for reproduction of material from all other RSC journals and books: Adapted from Ref. [41] with permission from The Royal Society of Chemistry; (d1), (d2), (d3), (d4), and (d5) are adapted from *Electrochim. Acta*, 201, M. Xu, Z.C. Wang, F.W. Wang, P. Hong, C.Y. Wang, X.M. Ouyang, C.G. Zhu, Y.J. Wei, Y.H. Hun, and W.Y. Fang, Fabrication of cerium doped Ti/nanoTiO$_2$/PbO_2 electrode with improved electrocatalytic activity and its application in organic degradation, 240-250, Copyright 2016, with permission from Elsevier.

possible reasons for the low service life of this electrode.

Numerous studies [7,46–49] have been carried out to solve these problems. A porous structure can significantly enhance the surface area, providing an active site for electrochemical reaction and improving the electrocatalytic performance. Meanwhile, the porous structure increases the contact area with the substrate, enhances the adhesion of the BDD film, and improves electrode stability. Fig. 6 displays several SEM images of the porous BDD electrode [7,46–48].

The intermediate layer of TiC, which has a rough and por-

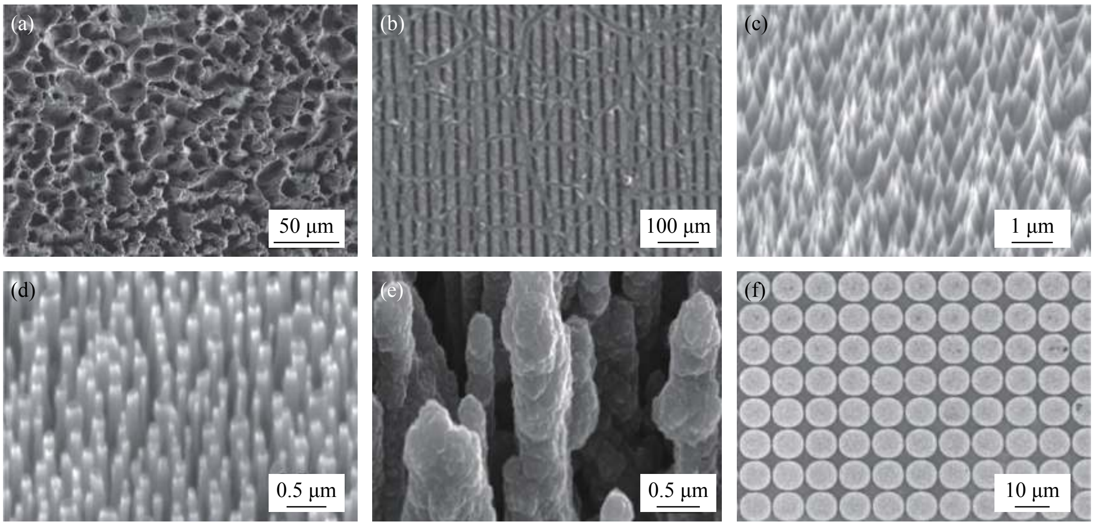


Fig. 6. SEM images of porous BDD electrodes: (a) teepee; (b) network; (c) nanocone array; (d) nanopillar array; (e) forest; (f) columnar array. (a) is reprinted with permission from H. Zanin, P.W. May, D.J. Fermin, D. Plana, S.M.C. Vieira, W.I. Milne, and E.J. Corat, *ACS Appl. Mater. Interfaces*, 6, 990-995 (2014) [46]. Copyright 2014 American Chemical Society; (b), (c), and (d) are reprinted from *Sep. Purif. Technol.*, 212, Y.P. He, H.B. Lin, Z.C. Guo, W.L. Zhang, H.D. Li, and W.M. Huang, Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants, 802-821, Copyright 2019, with permission from Elsevier; (e) is adapted with permission from D.B. Luo, L.Z. Wu, and J.F. Zhi, *ACS Nano*, 3, 2121-2128 (2009) [48]. Copyright 2009 American Chemical Society; (f) is reprinted from *Appl. Surf. Sci.*, 303, Y. Zhao, H.T. Yu, X. Quan, S. Chen, H.M. Zhao, and Y.B. Zhang, Preparation and characterization of vertically columnar boron-doped diamond array electrode, 419-424, Copyright 2014, with permission from Elsevier.

ous structure, will destroy the film adhesion of the Ti/BDD electrode [50]. Adjusting the number of diamonds in the BDD material can prevent TiC generation. The thickness of the TiC layer decreases with the increase in boron content, but the evolution of oxygen potential decreases with the increase in boron doping. Therefore, the content of boron should be controlled during BDD synthesis.

Several studies improved the stability of the BDD coating by adjusting and optimizing the deposition process parameters to reduce structural defects. Lu *et al.* [51] observed that the service life of the anode inc reased from 360 to 655 h after condition optimization. Guo and Chen [52] adopted a two-temperature stage hot-filament CVD method to fabricate a Ti/BDD electrode, and the service life increased from 244 to 804 h. Tian *et al.* [53] deposited a silicon layer on the Ti substrate with a thickness of 0.2–0.3 μm by evaporation technology. Compared with Ti/BDD, the durability of the Ti/Si/BDD electrode was improved because the Si intermediate layer restricted the formation of the TiC layer. Zhang *et al.* [45] fabricated a composite material of BDD and Ti powders. The experimental results showed that the service life of the composite material was prolonged from 295 to 500 h.

3.3.4. Stannic oxide

Pure SnO_2 is an n-type semiconductor material and has a wide bandgap of 3.8–4.3 V. It is usually doped with other elements to improve its electrical conductivity. Sb is the most commonly used doping element. The Ti/SnO_2–Sb electrode has the advantages of easy preparation and low cost. This electrode is a promising candidate for practical application in EO [54]. In general, the Ti/SnO_2–Sb electrode is prepared by electrodeposition, which is fit for large-scale yield. However, given the shortcomings of aqueous solvents and the weak adhesion between SnO_2 and the substrate, this electrode generally has weak electrochemical activity and short service life [55].

The SnO_2–Sb–X (X = Ir, Fe, Pt, Ni, etc.) electrode has an outstanding performance compared with the SnO_2–Sb electrode. Feng and his team [56–57] conducted considerable work focusing on the preparation and mechanism of introducing elements to the Ti/SnO_2–Sb electrode. Rare earth elements, including Ce, Eu, Gd, and Dy, were used for doping modification to degrade phenolic compounds. The results showed that Gd-doped Ti/SnO_2–Sb achieved the maximum degradation rate, whereas Ce-doped Ti/SnO_2–Sb attained the minimum rate. The microscopic lattice structure was analyzed, and the good performance may be due to the introduction of Gd, which reduced the oxygen vacancy of SnO_2 lattice species and enhanced the adsorption of •OH on the electrode surface, providing an environment conducive to the degradation of organic compounds.

In addition to co-doped SnO_2–Sb, other approaches have been proposed to improve electrode stability. Chen *et al.* [58] reported that the introduction of an interlayer to the coating can greatly increase the service life of electrodes. This finding is due to the prevention of intermediate layer to form an insulating layer of substrate, leading to low conductivity and poor stability during the electrochemical process. Zhao *et al.* [59] used a TiO_2 nanotube array to cover the Ti substrate surface, which increased the load capacity of the Ti/SnO_2–Sb electrode, improved the electrocatalytic activity, and prolonged the electrode service life from 22 to 42 h.

Other researchers [60–61] improved the performance of the Ti/SnO_2–Sb electrode by optimizing electrodeposition parameters, such as replacing water with colloidal solution, dimethyl sulfoxide solution, deep eutectic solvent (DES), etc. DES, given its biodegradable properties, is recognized as a green solvent and arouses wide concern in the electrochemical synthesis system [55,62].

3.3.5. Iridium oxide

IrO_2 has excellent conductivity and good corrosion resistance, and it is widely used as chlorine and oxygen evolution electrode. However, the disadvantages of low oxygen evolution potential and instability limit its development in sewage treatment. In recent years, to enhance the stability of IrO_2 coating and improve the electrochemical activity, researchers summarized the improved methods as follows: doping of elements (such as MnO_2, Ta_2O_5, SiO_2, etc.), addition of an intermediate layer, and nano-crystallization of crystal particles. Although the IrO_2 electrode has many defects in the application in water treatment, it exhibits high efficiency in the treatment of high-chlorine organic wastewater due to its low chlorine potential.

3.3.6. Comparison of different anode materials for EO degradation of phenolic compounds

The treatment efficiency and degradation pathway of phenolic compounds mainly depend on the nature of anode material. Comninellis [19] divided anodes into active and non-active electrode based on the strength of the interaction between •OH and the electrode. For active electrodes, the formation of oxide involves chemically adsorbed active oxygen, which has a strong interaction between •OH and electrodes.

For active electrodes, the degradation mechanism is mainly direct EO. Thus, the degradation efficiency mainly depends on electron transfer. In addition, severe fouling by toxic or refractory intermediates is the main bottleneck for the development of such electrode. In non-active anode materials, oxide formation involves the physically adsorbed active oxygen, which has a weak interaction between the electrode and •OH. Given the strong oxidizing property of •OH, the benzene ring easily opens, and phenolic compounds are directly mineralized to CO_2 and H_2O. Table 3 lists several anode materials with the oxidation potential and adsorption enthalpy of M–•OH [6].

Table 3. Oxidation potential and adsorption enthalpy of M–•OH of different anode materials. Adapted with permission from C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, and O. Scialdone, *Chem. Rev.*, 115, 13362-13407 (2015) [6]. Copyright 2015 American Chemical Society

Anode type	Composition	Oxidation potential / V	Adsorption enthalpy of M–•OH
Active	Ti/RuO_2	1.4–1.7	Chemisorption ↕ Physisorption
	Ti/IrO_2	1.5–1.8	
	Ti/Pt	1.7–1.9	
	Carbon and graphite	1.7	
Non-active	Ti/PbO_2	1.8–2.0	
	Ti/SnO_2–Sb	1.9–2.2	
	BDD	2.2–2.6	

Studies on the degradation of phenolic compounds should not only focus on the degradation efficiency but also on comprehending the degradation pathway and toxicity of intermediate compounds. Numerous researchers have studied the degradation of phenolic compounds using different anode materials. Quiroz *et al.* [24] used PbO_2, SnO_2, BDD, and $Ir_xRu_ySnO_2$ as anodic materials to research the electrocatalytic activity in the elimination of 1-hydroxy-2,4-dinitrobenzene. The order of electrocatalytic activity for removing 2,4-dinitrophenol (2,4-DNP) is as follows: Si/BDD >> $Ti/SnO_2 \geq Pb/PbO_2$ >> $Ti/Ir_{3/8}Ru_{1/8}Sn_{1/2}O_2 > Ti/Ir_{1/4}Ru_{1/4}Sn_{1/2}O_2$. The order of TOC removal can be arranged as Si/BDD >> $Pb/PbO_2 > Ti/SnO_2 > Ti/Ir_{3/8}Ru_{1/8}Sn_{1/2}O_2 > Ti/Ir_{1/4}Ru_{1/4}Sn_{1/2}O_2$. The non-active anode has a higher degradation rate for 2,4-DNP oxidation than the active anode. Meanwhile, the formation of intermediate compounds was also detected. For BDD anode, denitration is the first stage. Then, •OH attacks the phenol ring to form oxalic acid, finally followed by the generation of CO_2 and H_2O. For PbO_2 and SnO_2 anodes, several intermediates (such as p-nitrophenol, benzoquinone, malonic acid, oxalic acid, etc.) are produced via •OH attack on the phenol ring. For $Ir_xRu_ySnO_2$ anode, the intermediate is low-concentration polyhydroxyl. This finding can explain the difference in the TOC removal rate of different electrode materials. Barışçı *et al.* [63] examined the oxidation of phenol using different anodes, namely, Ti/IrO_2–RuO_2, Ti/RuO_2, Ti/IrO_2–Ta_2O_5, Ti/Ta_2O_5–SnO_2–IrO_2, and Ti/Pt. The order of the chemical oxygen demand (COD) removal rate is consistent with the oxygen evolution overpotential. Meanwhile, the degradation of intermediates shows a similar trend. Sun *et al.* [64] compared the degradation rate of phenol, COD removal rate, CE, EC, and intermediate products between PbO_2 and

BDD electrodes. The results showed that compared with the PbO_2, the BDD anode presented a higher degradation rate and CE and lower EC due to the high overpotential of oxygen evolution. Meanwhile, the quantities of PbO_2 intermediates were higher than those of the BDD anode, consistent with the lower degradation rate and CE of the PbO_2 electrode.

In conclusion, non-active anode materials with high oxygen overpotential easily open the benzene ring. They exhibit a high degradation rate and CE and low accumulation of intermediates. To support this conclusion, we collected a large number of active and non-active anodes for comparison. However, direct comparison of the degradation rates was difficult due to the various operating conditions of each experiment. Here, we calculated the degradation rate per coulomb to unify the result by using Eq. (7). The results are shown in Table 4. The non-active electrode has a higher degradation rate of phenolic compounds than the active electrode. Meanwhile, combined with the toxicity of intermediates, CE, and EC, the non-active electrode shows more advantages than the active electrode.

Table 4. Comparison of degradation rate per coulomb of phenol using different anode materials

Anode	C_0 / (mg·L^{-1})	V / mL	S / cm^2	I / (mA·cm^{-2})	t / min	Degradation rate / %	Y / (10^{-3} mg·C^{-1})	Ref.
Ti/Pt	100	350	25	31	480	99.5	1.56	[63]
Ti/RuO_2	100	350	25	31	480	87.1	1.37	[63]
Ti/IrO_2–RuO_2	100	350	25	31	480	84.7	1.33	[63]
Ti/IrO_2–Pt	8	1000	50	10	40	100	2.00	[65]
Ti/RuO_2–Pt	8	1000	50	10	30	100	2.67	[65]
Ti/SnO_2–Sb–Ni–Ce	50	60	8	20	120	96	2.50	[66]
PbO_2	50	200	1	20	180	73	33.80	[67]
Ti/TiO_2	300	500	10	25	540	80	14.81	[31]
TiO_2/activated carbon fiber	100	80	7.41	7.14	60	86	36.12	[68]
Blue-TiO_2 nanotubes anode	100	100	3	2.5	300	92	68.15	[69]
Ti/BDD	100	100	3	2.5	300	100	74.07	[69]

$$Y = \frac{C_0 \times V \times \text{degradation rate}}{I \times S \times t} \tag{7}$$

where Y is the degradation rate per coulomb; C_0 is the initial concentration of the phenolic compound (mg·L^{-1}); V is the volume of the solution (L); I is the current density (A·cm^{-2}); S is the electrode area (cm^2); t is the electrolysis time (s).

3.4. Type and concentration of electrolytes

In the EO process, the electrolyte is often added to the wastewater solution to improve conductivity. The commonly used electrolytes include Na_2SO_4, NaCl, NaBr, and KCl. The nature of electrolyte directly affects the degradation rate because strong oxidizing agents are present in the electrolyte, and these agents can be used as oxidants to degrade organic compounds. In parallel, SO_4^{2-} and Cl^- are regarded as quenchers that disrupt the reactions between •OH and organic compounds, as shown by Eqs. (8) and (9), respectively.

$$SO_4^{2-} + \bullet OH \rightarrow SO_4^{\bullet 2-} + OH^- \tag{8}$$

$$Cl^- + \bullet OH \rightarrow [ClOH]^{\bullet -} \tag{9}$$

Several studies [34,70] compared the degradation efficiency of phenol in NaCl and Na_2SO_4 electrolytes. The results showed that the degradation rate and COD removal rate in NaCl electrolyte are 2.26×10^{-2} and 3.00×10^{-4} min^{-1}, respectively, which are 9.5 and 1.5 times those of Na_2SO_4. These results are attributed to the higher removal rate for •OH of sulfuric acid than chloride. Other studies [71] compared the degradation efficiencies of phenol using NaCl and NaBr as electrolytes. Fig. 7 shows that the removal rate of bromide to phenol and TOC is better than that of chloride, because the reactivity and selectivity of active bromine are better than those of active chlorine. In addition, the degradation rate increases as the electrolyte concentration increases.

3.5. pH

Numerous studies reported the effects of pH solutions on the EO process. However, the results are diverse and contradictory because the oxidation capability of the oxidizing species changes depending on different pH. Several studies [72–74] pointed out that the degradation rate is higher when the pH is three compared with that at higher pH. Wang *et al.* [74] studied the effect of initial pH on the removal of phenol. The results showed that under acidic condition, phenol and TOC achieved a high removal rate because such condition inhibited the decomposition of •OH and oxygen. Meanwhile, Gao *et al.* [75] observed that the removal rates of phenol and TOC gradually increased with the decrease in pH. By comparison, Fadillah *et al.* [76] determined that pH = 11 was the optimal value for the degradation of 4-Nitrophenol (4-NP). They assumed the 4-NP molecule will hydrolyze in acidic solutions, resulting in changes in the surface electrical structure, which affect the degradation efficiency. However, under alkaline pH conditions, 4-NP ionizes and completely dissolves in the system, increasing the number of •OH formed

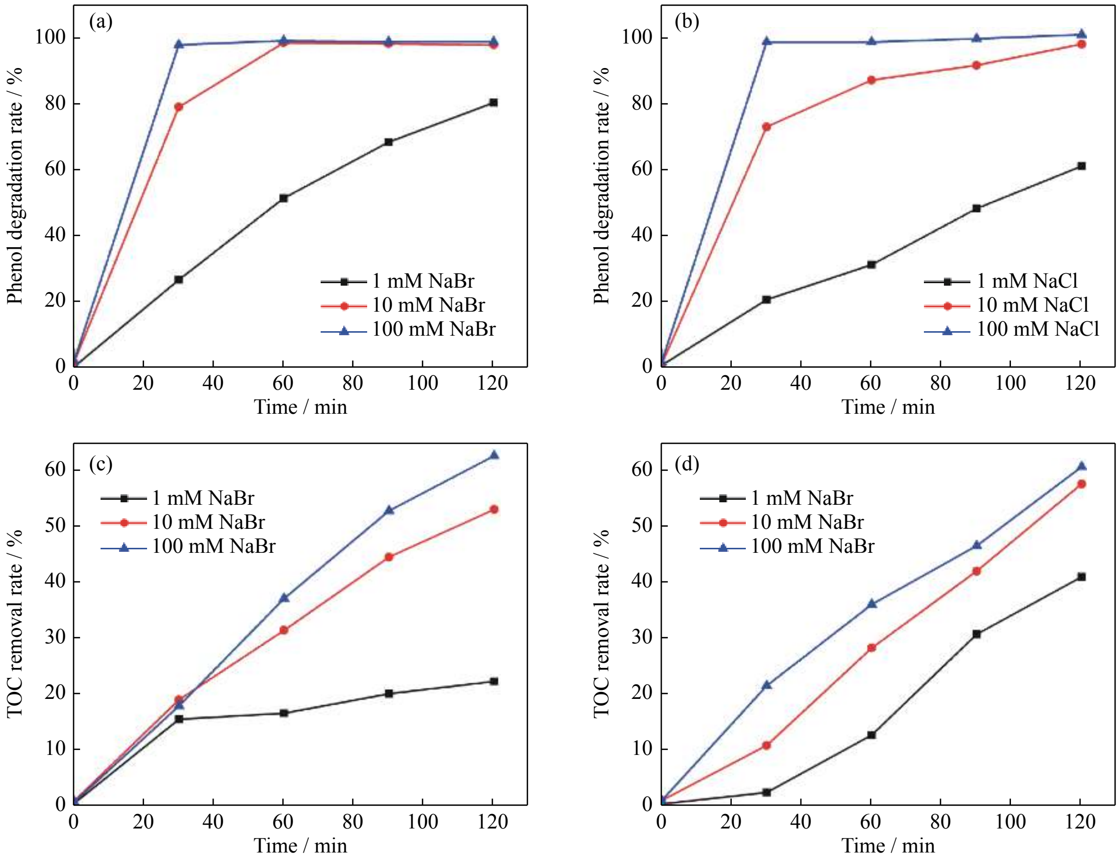


Fig. 7. Effects of electrolyte type and concentration on the degradation of phenol compounds: (a) effect of NaBr concentration on degradation of phenol; (b) effect of NaCl concentration on degradation of phenol; (c) effect of NaBr concentration on TOC removal rate; (d) effect of NaCl concentration on TOC removal rate. Adapted from *J. Hazard. Mater.*, 344, C.Y. Zhang, J.H. Xian, M. Liu, and D.G. Fu, Formation of brominated oligomers during phenol degradation on boron-doped diamond electrode, 123-135, Copyright 2018, with permission from Elsevier.

and improving the degradation process. The diversity of results may be due to the different catalytic activities of various oxidants or the varying stability of organic pollutants at different pH.

3.6. Initial organic concentration

Theoretically, the high initial concentration of organic compounds in wastewater will require considerable time to oxidize and degrade. However, several researchers [77–78] reported that high initial pollutant content leads to a high pollutant removal amount per unit time. This finding is due to the rapid oxidation of a large number of organic compounds by •OH. The progress of electrocatalytic wastewater treatment conforms to the pseudo-first-order kinetic model, and the reaction rate is theoretically independent of the reactant concentration. However, experiments [79–80] showed that increasing the concentration of reactants reduced the rate constant of the pseudo-first-order kinetics. This finding can be attributed to the transfer of the rate determination step from the diffusion process on the electrode to the charge transfer process at high initial organic pollutant concentrations.

3.7. Photo-EO process

In 1972, Fujishima and Honda [81] proposed that the TiO_2 electrode can decompose water under ultraviolet light. Thus, photocatalytic technology has become one of the research hotspots [82–84]. However, the charge recombination and low visible-light efficiency are bottlenecks in the development of photocatalytic technology [85]. A large number of studies revealed that in addition to the complementary advantages of selective oxidation capacity of electrocatalysis and photocatalysis, the existence of an electric field can greatly facilitate the separation of vacancy and electrons of photogenerated carriers and improve the photocatalytic efficiency. Villota-Zuleta *et al.* [86] treated phenol by photoelectrochemical technology; the results showed that the degradation rate of phenol is 73%, which is higher than that of photocatalytic (4.81%) and electrochemical (6.79%) processes. Hurwitz *et al.* [87] designed a photo-assisted electrochemical reactor to treat phenol using BDD or Ti/RuO_2 as anode. The results showed that the removal rate of photo-assisted electrochemical treatment reached 88% and 96% after 6 h, and these values are higher than that of photocatalytic treatment or electrochemical treatment alone. In addition, the cost effectiveness of photo-assisted electrochemical for mineralization was more than 75% higher than that of the photocatalytic process (50%). As a new water pollution control technology, photocatalytic technology can be applied in practice, depending on its high efficiency, stability, and operation cost. At present, photocatalytic technology is still limited to the laboratory stage, and is still far from industrial application.

3.8. Electrochemical reactor

The electrochemical reactor determines the mass transfer process of pollutants given that it is where the EO process is realized. The choice of reactor design is related to the composition and quantity of wastewater. Similar to all other chemical reactors, electrochemical reactors are operated in different modes. Fig. 8 shows several commonly used electrochemical reactors for EO degradation of organic compounds [88]. The main research direction of electrochemical degradation of organic matter is the selection and modification of electrode materials. However, the research on the improvement of reactor structure has been ignored in years.

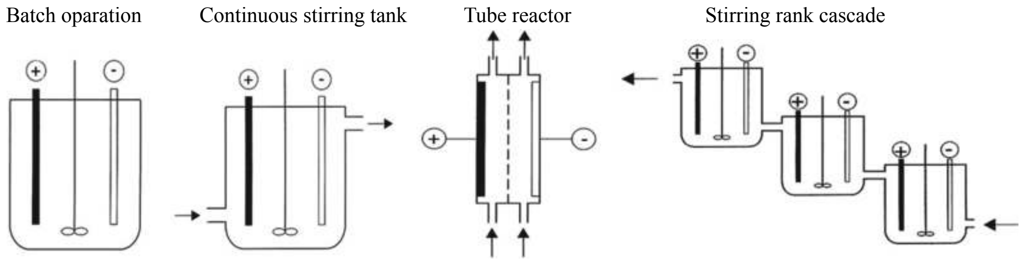


Fig. 8. Operating modes of electrochemical reactors for EO degradation of organic compounds [88].

4. Combination of EO technology with other processes for degradation of pollutants

Compared with other advanced oxidation technologies, EO technology has many advantages. However, it also presents disadvantages, such as high EC and operating costs. EO technology is used in combination with other treatment technologies, such as Fenton, biological, photocatalytic process, etc. to improve the degradation rate and reduce EC and toxic by-products.

4.1. Electrochemical–biological process

Given the toxic effect of phenolic compounds on organisms, EO is usually used as a pretreatment step to improve the suitability of organic compound degradation for biological systems and reduce costs. According to the report [89], the possibility of using biological technology to oxidize phenol to carbon dioxide is higher than that of 2-chlorophenol. Arellano-González *et al.* [90] first used EO to conduct a dichlorination reaction to convert 2-chlorophenol into phenol and then used a biological method to degrade the latter. Their study showed the similar times required for the mineralization of 2-chlorophenol using electrochemical biotechnology and electrochemical or advanced oxidation technology alone. However, the combined technology did not reduce the accumulation of by-products or excessive energy costs.

Electrolysis biofilm is another new electrochemical–biological technology that has gradually become a research hotspot. Zhang *et al.* [91] used a biofilm-electrode reactor to remove phenol. The reactor used Ti/PbO_2 as the anode and degrading bacteria fixed on the Ti electrode as the cathode. The degradation rate of phenol can reach 100% after 18 h, which is higher than that of biological or electrochemical method.

4.2. Electro-Fenton process

Electro-Fenton process is an electrochemical method that generates Fe^{2+} and H_2O_2, which are constant sources for Fenton reagents to generate •OH and then degrade organic matter [92]. Gümüş *et al.* [93] studied the effects of two different methods (Fenton and electro-Fenton methods) on phenol degradation. The results showed that the removal rates of phenol reached 93% in the electro-Fenton method and 59% in the Fenton method. The operation costs of the two methods were estimated, and the results showed that electro-Fenton process is more economical than the Fenton method alone.

5. Conclusion and perspectives

Phenolic compound treatment is one of the major challenges in wastewater treatment. EO is an effective method for phenolic compound treatment. As presented in this review, non-active electrodes are extremely promising for the treatment of phenolic compounds due to their high degradation rate, COD remove rate, and CE and low content of intermediate products. However, several problems need further investigation for the full development of the EO process.

(1) BDD and PbO_2 are commonly studied non-active electrode materials. BDD electrode has the advantages of high oxygen evolution potential and weak adsorption, and is the most promising electrode material for EO degradation of phenolic compounds. To date, the laboratory and pilot tests

of the BDD electrode have been successful, but its industrial application certain limitations, mainly because of the complex equipment, limited size, and high cost. Given the outstanding proprieties and numerous studies on the preparation methods, the industrial application of BDD will become inevitable in the future. PbO_2 is superior to other electrodes in terms of cost. However, the traditional PbO_2 active layer easily peels off, causing lead pollution in water and electrode damage. The use of PbO_2 in environmental applications in the future requires attention to electrocatalytic activity and stability. Meanwhile, a new alternative ideal electrode should be studied by further research on the structure and preparation method of electrode materials.

(2) The types and toxicity of intermediate products are important parameters. Studies on the degradation of phenolic compounds should not only pay attention to the degradation rate of phenols and COD removal rate but also to the understanding of the degradation pathway and toxicity of intermediate compounds. Meanwhile, studies should explore a stable and reliable detection method for •OH in electrochemical systems to gain insights into the degradation pathways of phenolic compounds.

(3) EO degradation of organic compounds should be promoted toward the direction of the realization of resource recovery, minimum EC, and complete mineralization. Thus, numerous additional technologies have been investigated for the improvement of CE and reduction of EC. Enhancing the coordination between EO and other technologies to improve the degradation rate and reduce the toxicity of intermediates are the focus of future research.

Acknowledgements

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