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Recent updates on electrochemical degradation of bio-refractory organic pollutants using BDD anode: a mini review

Xinmin Yu · Minghua Zhou · Youshuang Hu ·
K. Groenen Serrano · Fangke Yu

Abstract Boron-doped diamond (BDD) is playing an important role in environmental electrochemistry and has been successfully applied to the degradation of various bio-refractory organic pollutants. However, the review concerning recent progress in this research area is still very limited. This mini-review updated recent advances on the removal of three kinds of bio-refractory wastewaters including pharmaceuticals, pesticides, and dyes using BDD electrode. It summarized the important parameters in three electrochemical oxidation processes, i.e., anodic oxidation (AO), electro-Fenton (EF), and photoelectro-Fenton (PEF) and compared their different degradation mechanisms and behaviors. As an attractive improvement of PEF, solar photoelectro-Fenton using sunlight as UV/vis source presented cost-effectiveness, in which the energy consumption for enrofloxacin removal was 0.246 kWh/(g TOC), which was much lower than that of 0.743 and 0.467 kWh/(g TOC) by AO and EF under similar conditions. Finally the existing problems and future prospects in research were suggested.

Keywords Boron-doped diamond · Anodic oxidation · Electro-Fenton · Photoelectro-Fenton · Organic pollutant degradation

Introduction

Every year, thousands tons of organic pollutants are discharged into the environment, which have resulted in the pollution of soil, surface water, ground water, and even drinking water (Samet et al. 2010; Murugananthan et al. 2011; Cavalcanti et al. 2013). Though lots of these pollutants can be disposed effectively by conventional municipal sewage treatment plants, the emergence of some bio-refractory organic pollutants such as pharmaceuticals, pesticides, and synthetic dyes still brings huge challenges in treatment due to their widespread, toxic effect, and long-term adverse potential risks for the ecosystem, animals, and humans health even at trace levels (Domínguez et al. 2010; Flox et al. 2006). Therefore, it is urgent to develop sound treatment process to abate those pollutants with high efficiency.

Recently, advanced oxidation processes (AOPs) have been widely used to remove bio-refractory pollutants in wastewaters, with the common feature of in situ generation of hydroxyl radical ($\cdot\text{OH}$) which has so high standard redox potential ($E^0(\cdot\text{OH}/\text{H}_2\text{O})=2.80\text{ V vs SHE}$) that can react with most of the organic pollutants non-selectively up to mineralization (Skoumal et al. 2008). As one of the environmental-friendly technologies among AOPs, electrochemical oxidation possesses advantages of easy implementation, no chemicals addition, and high efficiency (Zhu et al. 2009; Brillas et al. 2009). Nevertheless, the large energy consumption is one of the main drawbacks of this method, and the development and improvement of new anode materials and cost-effective processes tend to relieve the problem (Aquino et al. 2011; Zhang et al. 2013).

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Generally, an ideal anode for pollutant degradation must have high O₂ evolution over-potential to diminish the side reactions of oxygen production (Chen et al. 2003). For this purpose, different kinds of anode materials have been tested, for example, Pt, IrO₂, RuO₂, SnO₂, and PbO₂ (Ciríaco et al. 2009; Frontistis et al. 2011). But because of some drawbacks such as low activity, low stability, and/or durability, these electrode materials are not adequate enough for electrochemical oxidation. Up to now, it has been widely recognized that diamond film has excellent properties of high resistance, high thermal conductivity, and high chemical stability (Wu et al. 2009). After boron-doped, the oxygen evolution potential and electrocatalytic performance of diamond film will be obviously improved, and the as-prepared boron-doped diamond (BDD) also has good conductive property and semiconductor property. So far, several materials (Si, Nb, Ta, W, and Ti) have been proved suitable for the deposition of BDD, and Si/BDD electrode is the most widely used in wastewater treatment in spite of the limits related to their industrial application owing to the fragility and the relatively low conductivity of the Si substrate (Chen 2004; Zhou et al. 2011). Compared with traditional electrode materials, BDD has many incomparably excellent characteristics, such as good chemical and electrochemical stability, strong corrosion resistant, high oxygen evolution potential (as high as 2.8 V), low background current, and wide electrochemical potential window (Wu et al. 2009; Martínez-Huitle and Brillas 2009; Sun et al. 2011, 2012).

Nowadays, diamond can be prepared under low pressure by chemical vapor deposition (CVD) methods with appropriate activation conditions, including the most common and effective hot-filament CVD (HFCVD) and microwave plasma-assisted CVD (MPCVD). Generally, the preparation procedure of BDD can be simplified as follows (Luong et al. 2009; Pecková et al. 2009): Carbon-containing gases such as CH₄ and CO are activated at high gas temperature (2,200–2,800 °C) and deposit on the target substrate (Si, Ti, and so on) under proper temperature, pressure, and reaction time. Boron doping is usually achieved by adding B₂H₆ or B(OCH₃)₃ to the gas stream or placing boron powder near the edges of the substrate prior to inserting into the CVD chamber. Although BDD preparation is a tedious work needing relatively large cost, BDD possesses some incomparable properties that mentioned above and thus has shown promising for the treatment of organic wastewater.

As an ideal anode material, BDD electrode has been applied to the removal of pollutants by various electrochemical technologies including anodic oxidation (AO), electro-Fenton (EF), and photoelectro-Fenton (PEF) (Liu et al. 2009; Sirés and Brillas 2012). This research area has attracted considerable interests; however, the review papers in recent years are still very limited (Panizza and Cerisola 2005; Quiroz Alfaro et al. 2006). Therefore, the present work is focused on the electrochemical degradation of pharmaceuticals, pesticides, and dyes using BDD electrode by anodic oxidation, electro-Fenton, and photoelectro-

Fenton, which would update the applications in recent years. It should be noted that the referred wastewaters in this work were all synthetic organic wastewaters.

Anodic oxidation

Among the electrochemical methods, anodic oxidation is perhaps the most popular one for the treatment of wastewaters containing persistent organic pollutants (POPs) (Brillas et al. 2010). The pollutants are supposed to be removed at a high oxygen evolution potential anode by the generated hydroxyl radicals ($\cdot\text{OH}$) (Panizza and Cerisola 2009; Moreira et al. 2013). When BDD is used, hydroxyl radical BDD($\cdot\text{OH}$) can be formed on the BDD surface (Eq. 1) (Isarain-Chávez et al. 2010). Thus, BDD is powerful enough to mineralize refractory pollutants and their degradation intermediates including carboxylic acids and possesses much higher oxidation power than other common anodes (Guinea et al. 2010).

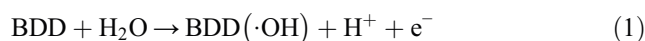


Table 1 lists the degradation of different organic pollutants by anodic oxidation, in which the TOC removal for pharmaceuticals, pesticides, and dyes differed much but the removal efficiency of pollutant was usually very high (>90 %). It can be seen that the substrate of BDD is usually silicon, but the cathode material was different. Graphite, platinum, dimensional stable electrode (DSA), stainless steel, and air diffusion electrode (ADE) are frequently used as cathodic materials. When graphite or ADE is used as cathode, it is often fed with air or pure oxygen to generate H₂O₂ through the electrochemical reduction of O₂. This process is called AO-H₂O₂ which also belongs to the scope of anodic oxidation. As to the supporting electrolyte, Na₂SO₄ is usually selected for the following reasons: (1) relatively cheap, (2) it could be oxidized into S₂O₈²⁻ which also participated in the degradation of organics, and (3) it would not produce hazardous compounds during treatment; the presence of Na₂SO₄ would promote degradation (Özcan et al. 2008).

Current density is one of the most important parameters in AO. As shown in Table 1, among the investigated ranges (10–500 mA/cm²), higher current density could lead to better treatment performance for pollutant or TOC removal, i.e., removal contaminants within less time or reaching higher removal within the same period. For instance, using bisphenol A of 20 mg/L as the model pollutant, it would require 10, 9, and 5 h for complete degradation of bisphenol A and 24, 16, and 14 h for complete removal of TOC when the applied current density was 14.28, 25, and 35.7 mA/cm², respectively (Murugananthan et al. 2008). Similar conclusions could be drawn on the degradation of methyl violet, in which the removal efficiency was 49, 92, and 97 % in 10 h and the

Table 1 Degradation of different organic pollutants by anodic oxidation

Pollutant	Initial concentration	Electrode	Other parameters	Electrolyte	Current/voltage	Pollutant removal	TOC removal	MCE	Reference
17-Estradiol (E2)	500 µg/L	Anode: Si/BDD (4 cm ²) Cathode: Pt (8 cm ²)	Batch pH=6.0 V=500 mL	0.1 M Na ₂ SO ₄	12.5 mA/cm ² 25 mA/cm ² 50 mA/cm ²	100 % (40 min) 100 % (40 min) 100 % (30 min)	58 % (4.5 h) 80 % (4.5 h) 94 % (4.5 h)	2.04–1.13 % – 1.02–0.874 %	Muruganathan et al. 2007
Atenolol	2.25 µM	Anode: Si/BDD (11.25 cm ²) Cathode: Pt	Batch pH=6.0 V=250 mL	0.1 M Na ₂ SO ₄	4.44 mA/cm ² 8.88 mA/cm ² 13.3 mA/cm ²	– – –	80 % (25 h) 96 % (25 h) 100 % (20 h)	– – –	Muruganathan et al. 2011
Chloroxylenol	100 mg/L	Anode: Si/BDD (3 cm ²) Cathode: stainless steel	Batch pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ² 100 mA/cm ² 150 mA/cm ²	100 % (420 min) 100 % (240 min) 100 % (180 min)	>96 % (5 h) >96 % (5 h) >96 % (5 h)	14 % (3 h) 5.5 % (3 h) 4.0 % (3 h)	Skoumal et al. 2008
Bisphenol A	20 mg/L	Anode: Si/BDD (7 cm ²) Cathode: Pt	Batch pH=6.0 V=250 mL	0.1 M Na ₂ SO ₄	14.28 mA/cm ² 25 mA/cm ² 35.7 mA/cm ²	100 % (10 h) 100 % (9 h) 100 % (5 h)	100 % (24 h) 100 % (16 h) 100 % (14 h)	3.4 % – 2.65 %	Muruganathan et al. 2008
Clofibrac acid	179 mg/L	Anode: Si/BDD (3 cm ²) Cathode: stainless steel	Batch pH=12 V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ² 100 mA/cm ² 150 mA/cm ²	100 % (540 min) 100 % (420 min) 100 % (360 min)	100 % (10 Ah/L) 100 % (21 Ah/L) 100 % (27 Ah/L)	– – –	Sirés et al. 2006
Diclofenac	175 mg/L	Anode: Si/BDD (3 cm ²) Cathode: stainless steel	Batch pH=6.5 V=100 mL	0.05 M Na ₂ SO ₄	50 mA/cm ² 100 mA/cm ² 300 mA/cm ² 450 mA/cm ²	93.1 % (360 min) 98.9 % (360 min) 100 % (300 min) 100 % (200 min)	78 % (6 h) 85 % (6 h) 97 % (6 h) 99 % (6 h)	– – – –	Brillas et al. 2010
Dipyrene	100 mg/L	Anode: Ti/BDD (14.4 cm ²) Cathode: DSA	Flow, flow rate—50 L/h V=2.0 L	0.1 M H ₂ SO ₄ 0.1 M K ₂ SO ₄	3.5 V 4.0 V 4.5 V 5.0 V	100 % (120 min) 100 % (90 min) 100 % (45 min) 100 % (25 min)	8 % 15 % 30 % 44 %	– – – –	Reis et al. 2013
Enrofloxacin	158 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ²	78 % (360 min)	>97 % (6 h)	–	Guinea et al. 2010
Ibuprofen	1.75 mM	Anode: Si/BDD (20 cm ²) Cathode: stainless steel foils	Batch	0.035 M Na ₂ SO ₄	10 mA/cm ² 20 mA/cm ² 30 mA/cm ²	– – –	85 % (6 h) 90 % (6 h) 95 % (6 h)	– – –	Ciriaco et al. 2009
Omeprazole	169 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=7.0 V=100 mL	0.05 M Na ₂ SO ₄	33.3 mA/cm ² 66.6 mA/cm ² 100 mA/cm ²	100 % (75 min) 100 % (80 min) 100 % (150 min)	45 % (6 h) 54 % (6 h) 78 % (6 h)	10 % (6 h) 6.0 % (6 h) 5.8 % (6 h)	Cavalcanti et al. 2013
Paracetamol	157 mg/L	Anode: Si/BDD (3 cm ²) Cathode: graphite	Batch pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	100 mA/cm ² 300 mA/cm ² 450 mA/cm ²	– 100 % (150 min) –	64 % (4 h) 91 % (4 h) 98 % (4 h)	15 % (4 h) 7.2 % (4 h) 5.2 % (4 h)	Brillas et al. 2005
4-CPA	100 mg/L (TOC)	Anode: Si/BDD (3 cm ²) Cathode: graphite bar	Batch pH=3	0.05 M Na ₂ SO ₄	33.3 mA/cm ² 100 mA/cm ²	100 % (540 min) –	54 % (3 h) 61 % (3 h)	16 % (3 h) 6.0 % (3 h)	Brillas et al. 2004

Table 1 (continued)

Pollutant	Initial concentration	Electrode	Other parameters	Electrolyte	Current/voltage	Pollutant removal	TOC removal	MCE	Reference
MCPA			$V=100$ mL		166.7 mA/cm ²	–	70 % (3 h)	4.6 % (3 h)	
					33.3 mA/cm ²	100 % (480 min)	58 % (3 h)	18 % (3 h)	
					100 mA/cm ²	–	61 % (3 h)	6.4 % (3 h)	
2,4-D					166.7 mA/cm ²	–	66 % (3 h)	6.6 % (3 h)	
					33.3 mA/cm ²	100 % (420 min)	57 % (3 h)	16 % (3 h)	
					100 mA/cm ²	–	70 % (3 h)	6.5 % (3 h)	
2,4,5-T					166.7 mA/cm ²	–	94 % (3 h)	5.8 % (3 h)	
					33.3 mA/cm ²	100 % (360 min)	59 % (3 h)	15 % (3 h)	
					100 mA/cm ²	–	–	–	
2,4-DP	217 mg/L	Anode: Si/BDD (17 cm ²) Cathode: graphite (3 cm ²)	Batch pH=3.0 $V=100$ mL	0.05 M Na ₂ SO ₄	166.7 mA/cm ²	–	77 % (3 h)	6.7 % (3 h)	Brillas et al. 2007
					100 mA/cm ²	100 % (300 min)	63 % (4 h)	14 %	
					300 mA/cm ²	–	82 % (4 h)	6.1 %	
Desmetryne	110 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 $V=100$ mL	0.05 M Na ₂ SO ₄	450 mA/cm ²	–	97 % (4 h)	4.8 %	Borràs et al. 2011
					100 mA	–	27 % (3 h)	9.9 %	
					300 mA	100 % (80 min)	60 % (3 h)	7.3 %	
Mecoprop	220 mg/ 440 mg/L		$V=100$ mL		450 mA	–	68 % (3 h)	5.5 %	
					300 mA	–	51 % (3 h)	12.3 %	
					300 mA	–	49 % (3 h)	23.7 %	
Propham	0.5 mM	Anode: Nb/BDD Cathode: Pt gauze	Flow, flow rate—130 L/h pH=3.0 $V=1.8$ L	0.05 M Na ₂ SO ₄	50 mA/cm ²	100 % (15 min)	100 % (14 Ah/L)	–	Flox et al. 2006
					100 mA/cm ²	100 % (15 min)	100 % (18 Ah/L)	–	
					150 mA/cm ²	100 % (17 min)	100 % (27 Ah/L)	–	
Cyanazine	55 mg/L 110 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 $V=0.15$ L	0.1 M NaNO ₃ 0.1 M LiClO ₄ 0.1 M NaCl	30 mA	100 % (180 min)	62 % (3 h)	77.68 % (180 min)	Özcan et al. 2008
					50 mA	100 % (180 min)	77 % (3 h)	58.44 % (180 min)	
					100 mA	100 % (180 min)	84 % (3 h)	31.72 % (180 min)	
					300 mA	100 % (180 min)	94 % (3 h)	11.92 % (180 min)	
					500 mA	100 % (180 min)	95 % (3 h)	7.2 % (180 min)	
					100 mA	100 % (180 min)	43 % (3 h)	16.22 % (180 min)	
Acid black 210	145 mg/L 500 mg/L	Anode: Si/BDD (20 cm ²) Cathode: stainless steel	Flow, flow rate—90 L/h pH=6.8	0.20 mol phosphate buffer	100 mA/cm ²	–	68 % (4 h)	2.8 % (4 h)	Borràs et al. 2013
					33.3 mA/cm ²	–	37 % (4 h)	8.9 % (4 h)	
					100 mA/cm ²	91 % (60 min)	66 % (4 h)	5.2 % (4 h)	
					150 mA/cm ²	–	69 % (4 h)	3.7 % (4 h)	
					100 mA/cm ²	–	59 % (4 h)	6.1 % (4 h)	
					50 mA/cm ²	–	74 % (3 h)	–	

Table 1 (continued)

Pollutant	Initial concentration	Electrode	Other parameters	Electrolyte	Current/voltage	Pollutant removal	TOC removal	MCE	Reference
Methyl orange	50 mg/L	Anode: Si/BDD (3 cm ²) Cathode: stainless steel	<i>V</i> =250 mL	0.1 M Na ₂ SO ₄ 0.1 M Na ₂ SO ₄ & 0.05 M NaCl	100 mA/cm ²	–	100 % (3 h)	–	Zhou et al. 2011
			Batch pH=3.0		50 mA/cm ²	–	25 %	–	
Methyl violet	200 mg/L (TOC)	Anode: Si/BDD (3 cm ²) Cathode: stainless steel	<i>V</i> =200 mL	0.05 M Na ₂ SO ₄	33.3 mA/cm ²	49 % (600 min)	56 % (4 h)	42 % (max)	Hamza et al. 2009
			Batch pH=3.0		100 mA/cm ²	92 % (600 min)	83 % (4 h)	27 % (max)	
Orange II	750 mg/L	Anode: Ti/BDD	<i>V</i> =100 mL	2 g/L Na ₂ SO ₄	150 mA/cm ²	97 % (600 min)	90 % (4 h)	17 % (max)	Chen and Chen 2006
			Flow		100 A/m ²	–	97 % (COD)	58.3 %	
		Cathode: stainless steel	200 A/m ²	–	92 % (COD)	54.9 %			
			Batch pH=8.5	400 A/m ²	–	84 % (COD)	50.7 %		
Reactive Orange 16	85 mg/L	Anode: Si/BDD (1.44 cm ²) Cathode: Pt foil (2 cm ²)	<i>V</i> =35 mL	0.1 M Na ₂ SO ₄	100 A/m ²	–	82 % (COD)	–	Migliorini et al. 2011
			Flow, flow rate—7 L/min pH=5.6		10 mA/cm ²	60 % (0.25 Ah/L)	–	–	
			<i>V</i> =300 mL	0.05 M NaCl	50 mA/cm ²	100 % (0.10 Ah/L)	–	–	
Reactive Blue 19	50 mg/L	Anode: Ti/BDD (5 cm ²) Cathode: Pt wire	Batch	0.023 M Na ₂ SO ₄	70 mA/cm ²	100 % (0.06 Ah/L)	–	–	Petrucci and Montanaro 2011
					200 A/m ²	100 % (90 min)	75 % (410 min)	–	
					300 A/m ²	100 % (60 min)	75 % (370 min)	–	
Remazol Brilliant Blue	50 mg/L	Anode: Si/BDD (5 cm ²) Cathode: Pt wire	Batch pH=5.8	0.05 M Na ₂ SO ₄ 0.01 M NaCl	600 A/m ²	100 % (30 min)	75 % (260 min)	–	Montanaro and Petrucci 2009
					200 A/m ²	100 % (10 min)	45 % (160 min)	–	
					300 A/m ²	100 % (8 min)	70 % (160 min)	–	
Sunset Yellow FCF	290 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	<i>V</i> =100 mL	0.05 M Na ₂ SO ₄	400 A/m ²	100 % (7 min)	100 % (160 min)	–	Moreira et al. 2013
			Batch pH=3.0		16.7 mA/cm ²	–	45 % (3 Ah/L)	–	
			<i>V</i> =100 mL		33.3 mA/cm ²	95 % (360 min)	70 % (3 Ah/L)	–	
					100 mA/cm ²	–	85 % (3 Ah/L)	–	

TOC removal was 56, 83, and 90 % in 4 h when the current density was 33.3, 100, and 150 mA/cm², respectively (Hamza et al. 2009).

Although higher current density can lead to higher pollutant and TOC removal, the applied current density should not be too high because higher current density can also cause higher energy consumption and lower mineralization current efficiency (MCE) which could be calculated by Eq. 2,

$$\text{MCE (\%)} = \frac{nFV\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 mIt} \times 100 \quad (2)$$

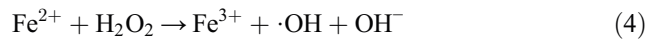
where F is the Faraday constant (96,485 C/mol), V is the solution volume (L), $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC removal, 4.32×10^7 is a conversion factor (3,600 s/h \times 12,000 mg/mol), m is the number of carbon atoms of the pollutant, I is the applied current (A), t is the electrolysis time (h), and n is the number of electrons. Taken the degradation of cyanazine as an example, it was not hard to find out that the MCE declined gradually when the current density increased. At 240 min, the MCE was 8.9, 5.2, and 3.7 %, respectively, when the current density was 33.3, 100, and 150 mA/cm² (Borràs et al. 2013). This phenomenon can be explained by the acceleration of generating other weak oxidants such as $\text{S}_2\text{O}_8^{2-}$ ($2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{e}^-$) and the rise of side reactions such as oxygen evolution reaction. In addition, the increase of current density can also result in the detriment of the main oxidant hydroxyl radical. So it is necessary to seek out an optimal current density to balance the energy consumption and current efficiency.

It is very important to summarize the influence of initial concentration on the removal performance of pollutants. As a general rule, with the increase of the initial concentration of organics, the removal efficiency decreases, no matter the pollutant or TOC removal, but the MCE increases (Borràs et al. 2011, 2013). As far as the removal of desmetryne, the TOC removal was 60, 51, and 49 % in 3 h, and the MCE was 7.3, 12.3, and 23.7 % when the initial concentration of desmetryne was 110, 220, and 440 mg/L, respectively (Borràs et al. 2011). So when the initial concentration of pollutants in wastewater was too high and even surpassed a certain value, the mineralization extent of organic pollutants would be incomplete, requiring a longer treatment time or pretreatment in advance to attain complete oxidation.

Electro-Fenton

Electro-Fenton is known as an indirect electro-oxidation treatment based on the combined usage of H_2O_2 and Fe^{2+} as catalyst (Sirés et al. 2007a; Brillas et al. 2009). In this process, H_2O_2 is continuously supplied into the contaminated

wastewaters by the cathodic two-electron reduction of O_2 (Eq. 3) (Murugananthan et al. 2011; Brillas et al. 2009). The generated H_2O_2 and the added Fe^{2+} then react with each other to produce $\cdot\text{OH}$ from Fenton's reaction (Eq. 4). This reaction is catalytic and can be propagated by the reduction of Fe^{3+} to Fe^{2+} occurred on the cathode (Eq. 5) (Borràs et al. 2013). In addition, the sparged O_2 could also be transformed into $\cdot\text{O}_2^-$ radical ($E^0 = -0.33$ V/NHE) in cathode compartment (Eq. 6) (Irmak et al. 2006).



The choice of electrode material is very important for EF process. It has been confirmed that carbonaceous material, for example, reticulated vitreous carbon, graphite felt, carbon felt, activated carbon fiber, and ADE, has the ability to generate enough H_2O_2 (Skoumal et al. 2008; Zhou et al. 2013). Among these cathodes, ADE fed with air or pure oxygen can achieve a high H_2O_2 production in acidic medium. The removal performance of EF process can be greatly improved by using BDD as anode instead of some common anode materials such as DSA. In this case, $\cdot\text{OH}$ is formed in two different ways: One is produced on the surface of BDD, and the other is formed via electro-Fenton reaction (Oturán et al. 2011). As a result, the generation rate of $\cdot\text{OH}$ is enhanced and thus promotes the oxidation of pollutants.

As an environmental friendly technique, EF is attracting more and more attention for wastewater treatment. From Table 2, it can be noticed that ADE is the most widely used cathode, though carbon felt is also very common in the EF process. Similar to AO process, Na_2SO_4 is also usually chosen as the supporting electrolyte for EF. In common circumstance, acidic environment (pH 2 to 4) is favorable for EF.

In fact, current density is also a very important parameter for EF, and its impact on the removal efficiency and MCE is as the same as those in AO. In degradation of chlorophene by EF, the TOC removal efficiency was 33, 45, 85, and 97 % in 11 h, and the MCE was 19, 14, 12, and 10 % in 60 min when the applied current density was 60, 100, 200, and 300 mA/cm², respectively (Sirés et al. 2007a). The improvement of removal efficiency with current density was attributed to the production of higher amounts of $\cdot\text{OH}$ due to the quicker generation of

Table 2 Degradation of different organic pollutants by electro-Fenton

Pollutant	Initial concentration	Electrode	Other parameter	Electrolyte	Current/voltage	Fe ²⁺ /Fe ³⁺ (mM)	Pollutant removal	TOC removal	MCE	Reference
Ibuprofen	41 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=100 mL	0.05 M Na ₂ SO ₄	3.3 mA/cm ²	0.5	—	68 % (DOC, 6 h)	—	Ciriaco et al. 2009
					13.3 mA/cm ²		—	92 % (DOC, 6 h)	—	
					33.3 mA/cm ²		100 % (30 min)	92 % (DOC, 6 h)	4.7–8.7 %	
Enrofloxacin	158 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ²	0.1 0.2 0.5	—	59 % (4 h)	—	Guinea et al. 2010
					—		—	64 % (4 h)	—	
					—		—	67 % (4 h)	—	
Chlorophene	84 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=200 mL	0.05 M Na ₂ SO ₄	60 mA/cm ²	4.0 (Fe ³⁺)	—	33 % (11 h)	19 % (60 min)	Sirés et al. 2007a
					100 mA/cm ²		—	45 % (11 h)	14 % (60 min)	
					200 mA/cm ²		—	85 % (11 h)	12 % (60 min)	
Chloroxylenol	100 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ²	1.0	100 % (90 min)	97 % (11 h)	10 % (60 min)	Skoumal et al. 2008
					—		100 % (20 min)	82 %	24 % (max)	
					—		—	—	—	
Atenolol	158 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=100 mL	0.05 M Na ₂ SO ₄	50 mA	0.5	88 % (60 min)	77 % (360 min)	18–50 % (360 min)	Muruganathan et al. 2011
					—		—	—	—	
					—		—	—	—	
Propranolol	154 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—20 mL/min V=100 mL	0.05 M Na ₂ SO ₄	10 mA/cm ²	0.5	—	78 % (420 min)	75 % (max)	Isarain-Chávez et al. 2010
					20 mA/cm ²		—	80 % (420 min)	47 % (max)	
					40 mA/cm ²		100 % (29 min)	85 % (420 min)	24 % (max)	
					60 mA/cm ²		—	88 % (420 min)	16 % (max)	
Sulfamethazine	193 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 Air flow rate—300 mL/min V=100 mL	0.05 M Na ₂ SO ₄	33.3 mA/cm ²	0.5	100 % (20 min)	81 % (DOC, 420 min)	—	El-Ghenymy et al. 2013
					66.7 mA/cm ²		100 % (10 min)	90 % (DOC, 420 min)	—	
					100 mA/cm ²		100 % (5 min)	94 % (DOC, 420 min)	—	
Sulfamethoxazole	0.208 mM	Anode: Nb/BDD (25 cm ²) Cathode: carbon felt	Batch pH=3.0 Air flow rate—1.0 L/min V=220 mL	0.05 M Na ₂ SO ₄	30 mA	0.2	—	86 % (600 min)	—	Dirany et al. 2010
					60 mA		100 % (25 min)	88 % (600 min)	—	
					100 mA		100 % (20 min)	94 % (600 min)	—	
					200 mA		100 % (15 min)	96 % (600 min)	—	
Triclosan	50 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 O ₂ flow rate—12 mL/min V=200 mL	0.05 M Na ₂ SO ₄	60 mA	0.2	100 % (120 min)	—	—	Sirés et al. 2007b
					300 mA		100 % (90 min)	—	—	
					60 mA		100 % (120 min)	—	—	
Triclocarban	5 mg/L	—	—	—	—	—	—	—	—	
Atrazine	0.20 mM	Anode: Si/BDD (15 cm ²)	Batch pH=3.0	0.05 M Na ₂ SO ₄	250 mA	0.1	—	48 % (2 h)	—	Balci et al. 2009

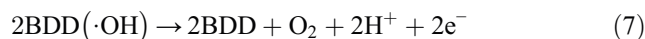
Table 2 (continued)

Pollutant	Initial concentration	Electrode	Other parameter	Electrolyte	Current/voltage	Fe ²⁺ /Fe ³⁺ (mM)	Pollutant removal	TOC removal	MCE	Reference		
2,4-DP	217 mg/L	Cathode: carbon felt	Air flow rate—1 L/min <i>V</i> =150 mL	0.05 M Na ₂ SO ₄	100 mA/cm ²	1.0	—	72 % (5 h)	—	Brillas et al. 2007		
		Anode: Si/BDD (10 cm ²)	Batch O ₂ flow rate—20 mL/min				300 mA/cm ²	—	82 % (10 h)		—	
		Cathode: ADE	pH=3.0 <i>V</i> =100 mL				450 mA/cm ²	—	82 % (4 h)		18 % (4 h)	
Cyanazine	55 mg/L 110 mg/L	Anode: Si/BDD (3 cm ²)	Batch pH=3.0	0.05 M Na ₂ SO ₄	100 mA/cm ² 33.3 mA/cm ²	0.5	—	87 % (240 min)	3.5 % (4 h)	Borràs et al. 2013		
		Cathode: ADE	O ₂ flow rate—20 mL/min <i>V</i> =100 mL				100 mA/cm ² 150 mA/cm ²	—	47 % (240 min)		11.3 % (4 h)	
								95 % (60 min)	82 % (240 min)		6.6 % (4 h)	
Desmetryne	55 mg/L 110 mg/L	Anode: Si/BDD (3 cm ²)	Batch O ₂ flow rate—12 mL/min	0.05 M Na ₂ SO ₄	300 mA 100 mA	0.5	—	68 % (3 h)	4.1 % (3 h)	Borràs et al. 2011		
		Cathode: ADE	pH=3.0 <i>V</i> =100 mL				450 mA	—	36 % (3 h)		13.1 % (3 h)	
							300 mA	—	100 % (45 min)		78 % (3 h)	9.5 % (3 h)
Acid Yellow 36	80 mg/L	Anode: Si/BDD (2 cm ²)	Batch pH=3.0	0.05 M Na ₂ SO ₄	8 mA/cm ² 15 mA/cm ²	0.3	95.2 %	—	—	Ruiz et al. 2011		
		Cathode: Si/BDD	Air flow rate—1 L/min <i>V</i> =100 mL				23 mA/cm ²	—	98.7 %		—	
								94.1 %	—		—	
	108 mg/L	Anode: Si/BDD (20 cm ²)	Flow pH=3.0	0.1 M Na ₂ SO ₄	0.5 A 1 A	0.5	—	46 % (360 min)	56 % (max)			
		Cathode: ADE	Liquid flow rate—200 L/h <i>V</i> =2.5 L				2 A 3 A	—	100 % (27 min)		54 % (360 min)	45 % (max)
								—	61 % (360 min)		32 % (max)	
	40 mg/L	Anode: Si/BDD (0.785 cm ²)	Batch	—	Anodic potential—2.5 v	1	94 % (180 min)	—	—			
		Cathode: Pt wire				6	69 % (180 min)	—	—			
						8	69 % (180 min)	—	—			
Direct Yellow 4	200 mg/L	Anode: Si/BDD (3 cm ²)	Batch pH=3.0	0.05 M Na ₂ SO ₄	25 mA/cm ² 33.3 mA/cm ²	0.5	—	68 % (240 min)	—	Garcia-Segura et al. 2012		
		Cathode: ADE	Air flow rate—0.3 mL/min <i>V</i> =100 mL				66.6 mA/cm ² 100 mA/cm ²	—	74 % (240 min)		—	
								—	85 % (240 min)		—	
4-CPA	100 mg/L (TOC)	Anode: Si/BDD (3 cm ²)	Batch	0.05 M NaSO ₄	33.3 mA/cm ² 100 mA/cm ²	0.5	100 % (15 min)	75 % (3 h)	22 % (3 h)	Brillas et al. 2004		
			O ₂ flow rate—20 mL/min				166.7 mA/cm ²	—	80 % (3 h)		7.9 % (3 h)	
MCPA		Cathode: ADE	pH=3.0		100 mA/cm ²		—	87 % (3 h)	5.7 % (3 h)			
							166.7 mA/cm ²	—	87 % (3 h)		9.1 % (3 h)	
2,4-D					33.3 mA/cm ²		100 % (12 min)	78 % (3 h)	22 % (3 h)			

Table 2 (continued)

Pollutant	Initial concentration	Electrode	Other parameter	Electrolyte	Current/voltage	Fe ²⁺ /Fe ³⁺ (mM)	Pollutant removal	TOC removal	MCE	Reference
2,4,5-T			V= 100 mL		100 mA/cm ² 166.7 mA/cm ² 33.3 mA/cm ² 100 mA/cm ² 166.7 mA/cm ²		— — 100 % (10 min) — —	90 % (3 h) 99 % (3 h) 80 % (3 h) 89 % (3 h) 97 % (3 h)	8.4 % (3 h) 6.1 % (3 h) 21 % (3 h) 7.7 % (3 h) 5.6 % (3 h)	
Sunset Yellow FCF	290 mg/L	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch pH=3.0 V= 100 mL	0.05 M Na ₂ SO ₄	16.7 mA/cm ² 33.3 mA/cm ² 100 mA/cm ²	0.5	— 100 % (26 min) —	75 % (3 Ah/L) 85 % (6 Ah/L) 90 % (18 Ah/L)	— — —	Moreira et al. 2013

H₂O₂ of reaction (3) at the ADE cathode and BDD(·OH) by increasing the rate of reaction (1). As to the decrease of MCE, there were also some reasons. The waste reactions involve the oxidation of BDD(·OH) to O₂ by reaction (7), as well as the dimerization of ·OH to H₂O₂ by reaction (8) or its destruction with H₂O₂ and Fe²⁺ by reactions (9) and (10), respectively. Moreover, the relative proportion of generated BDD(·OH) can also be reduced by the formation of weaker oxidants such as S₂O₈²⁻ by reaction (11) and ozone by reaction (12) (Isarain-Chávez et al. 2010)



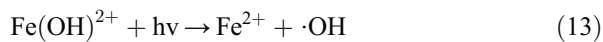
Theoretically, the removal performance of EF is better than AO under similar conditions due to two sources for the production of ·OH. This has been verified by degradation of several pollutants in these two systems under similar conditions. The initial TOC concentrations of 4-chlorophenoxyacetic acid (4-CPA), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4-dichlorophenoxyacetic acid (2,4-D), and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were all 100 mg/L, and Si/BDD was both used as the anode in two systems, while graphite bar and ADE were used as cathode in AO and EF system, respectively. 4-CPA, MCPA, 2,4-D, and 2,4,5-T can be completely removed in 540, 480, 420, and 360 min in AO system while in EF system the required time dramatically decreased to 15, 30, 12, and 10 min when the applied current density was 33.3 mA/cm². The MCE was 16, 6.5, and 5.8 % in AO system and enhanced to 22, 8.4, and 6.1 % in EF system when the applied current was 33.3, 100, and 166.7 mA/cm², respectively (Brillas et al. 2004). So such EF process using BDD is more promising for application due to the combination of AO and Fenton reaction, achieving a higher removal performance and MCE. Thus, this method can

also achieve relatively satisfactory results for the degradation of relatively high concentrated pollutants (Borràs et al. 2011).

Photoelectro-Fenton

In PEF process, the removal performance of organic pollutants by EF is enhanced by irradiation with either artificial UVA light or sunlight simultaneously (Almeida et al. 2012). Two main processes can explain the catalytic roles of UVA light:

1. The photo-reduction of $\text{Fe}(\text{OH})^{2+}$, which is the predominant Fe(III) species in pH range 2.5–4.0, regenerating greater amount of Fe^{2+} and producing more quantity of $\cdot\text{OH}$ via reaction (13) (Ruiz et al. 2011):



2. The quick photolysis of Fe(III)–carboxylate complexes, taken oxalic acid as example; the forms of Fe(III)–carboxylate complexes are $\text{Fe}(\text{C}_2\text{O}_4)^+$, $\text{Fe}(\text{C}_2\text{O}_4)_2^-$, and $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, and these complexes can be mineralized according to reaction (14) under irradiation (Ciriaco et al. 2009):

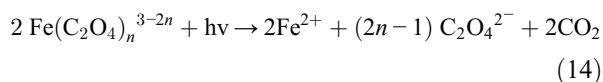


Figure 1 shows a general degradation pathway of aromatic organic pollutants by AO, EF, or PEF process (Brillas et al. 2004; Murugananthan et al. 2008). The target pollutant was firstly attacked by BDD($\cdot\text{OH}$) and $\cdot\text{OH}$, and as a result, it was degraded into some aromatic derivatives and further induced the cleavage of the benzene ring to form some typical acids such as acetic acid, maleic acid, and fumaric acid, which could be further transformed into oxalic acid and formic acid. These pathways mentioned above were all occurred in all three AO, EF, and PEF processes. In AO process, oxalic acid and formic acid were difficult to be removed and remained as the main products, resulting in the relatively low TOC removal efficiency. In EF process, refractory Fe(III)–carboxylate complexes could be formed due to the addition of Fe^{3+} , which could not be further degraded by $\cdot\text{OH}$ and thus inhibited the TOC removal. But these complexes could be photolyzed by UVA light in PEF, so PEF could produce more amount of Fe^{2+} and $\cdot\text{OH}$ which accelerated the Fenton reaction and the oxidation of organic pollutants. As a result, it could obtain the best removal performance in PEF system than that in EF or AO system.

Tables 1, 2, and 3 all exhibit the removal performance of 2,4-DP (initial concentration 217 mg/L) using Si/BDD as the

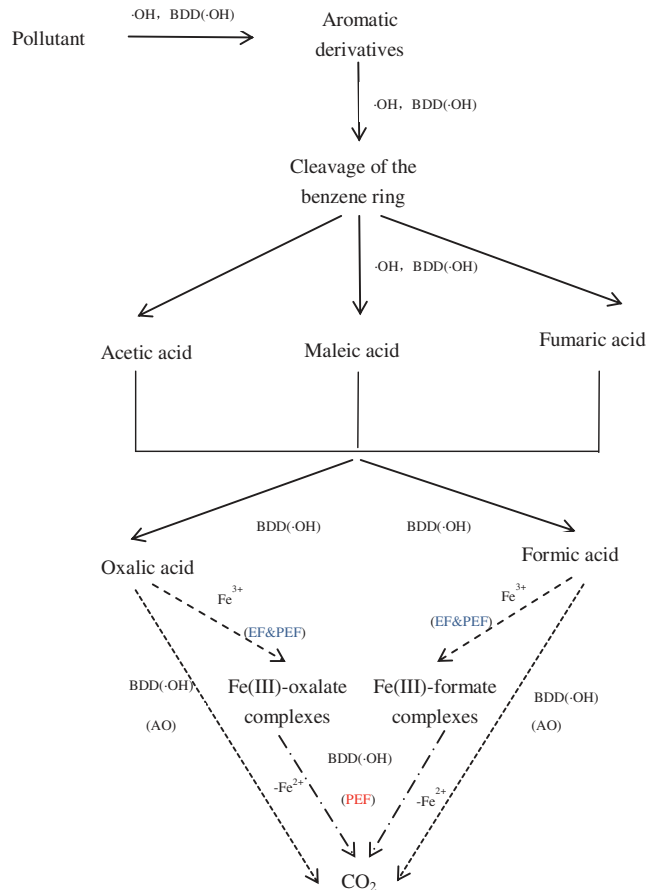


Fig. 1 A general pathway for aromatic pollutant degradation by AO, EF, and PEF

anode under similar conditions. For AO system, the cathode material was graphite; for EF and PEF, the added amounts of Fe^{2+} were 1.0 mM, and the oxygen flow rate was 20 mL/min as ADE was used as the cathode. For the PEF trials, a Philips 6-W fluorescent black light blue tube ($\lambda_{\text{max}}=360 \text{ nm}$) was placed at the top of the open cell, supplying a photoionization energy input of $140 \mu\text{W}/\text{cm}^2$ to the solution. 2, 4-DP could be completely removed within 300 min in AO system, but it was only reduced to 25 and 20 min in EF and PEF system, respectively, when the applied current density was $100 \text{ mA}/\text{cm}^2$. After 4 h, the TOC removal was 63, 82, and 97 % in AO system; 82, 88, and 97 % in EF system; and 83, 93, and 98 % in PEF system at the current density of 100, 300, and $450 \text{ mA}/\text{cm}^2$. In addition, when the current density was $100 \text{ mA}/\text{cm}^2$, the MCE of PEF and EF was both 18 %, but in AO system, it was only 14 % (Brillas et al. 2007).

Although the PEF process seems preferable to the AO and EF, its application for water treatment in large-scale system is limited by the high energy requirements of both the electrochemical cell and the artificial UVA lamp (Garcia-Segura et al. 2012). Recently, a much more economic PEF process, solar photoelectro-Fenton (SPEF), has been developed using sunlight as a free and renewable UV/Vis source. The very positive

Table 3 Degradation of different organic pollutants by photoelectro-Fenton

Pollutant	Initial concentration (mg/L)	Electrode	Other parameter	Electrolyte	Current/voltage	Fe ²⁺ /Fe ³⁺ (mM)	Pollutant removal	TOC removal	MCE	Reference
Atenolol	158	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	50 mA	0.5	100 % (30 min)	>95 % (360 min)	94 % (max)	Murugananthan et al. 2011
Clofibric acid	179	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch O ₂ flow rate—12 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ²	1.0	100 % (15 min)	>95 % (300 min)	31 % (max)	Sirés et al. 2006
					100 mA/cm ²	—	>95 % (300 min)	—		
					150 mA/cm ²	—	>95 % (300 min)	—		
Enrofloxacin	158	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33 mA/cm ²	0.2	100 % (20 min)	96 % (4 h)	44 % (max)	Guinea et al. 2010
Ibuprofen	41	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	6.6 mA/cm ²	0.5	100 % (60 min)	52 % (1.5 h)	—	Ciríaco et al. 2009
					13.3 mA/cm ²	100 % (50 min)	55 % (1.5 h)	—		
					33.3 mA/cm ²	100 % (40 min)	58 % (1.5 h)	14 % (max)		
Propranolol	154	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	10 mA/cm ²	0.5	—	96 % (4 h)	114 % (max)	Isarain-Chávez et al. 2010
					40 mA/cm ²	100 % (21 min)	96 % (3 h)	65 % (max)		
					33.3 mA/cm ²	100 % (10 min)	86 % (6 h)	71 % (max)	El-Ghenmy et al. 2013	
Sulfamethazine	193	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch Air flow rate—300 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33.3 mA/cm ²	0.5	100 % (8 min)	96 % (6 h)	42 % (max)	
					100 mA/cm ²	100 % (6 min)	97 % (6 h)	32 % (max)		
					100 mA/cm ²	100 % (4 h)	91 % (4 h)	3.7 % (4 h)	Borràs et al. 2013	
Cyanazine	55	Anode: Si/BDD 3 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	100 mA/cm ²	0.5	—	91 % (4 h)	3.7 % (4 h)	
	110				33.3 mA/cm ²	—	45 % (4 h)	10.8 % (4 h)		
					100 mA/cm ²	100 % (40 min)	90 % (4 h)	7.2 % (4 h)		
145	Cathode: ADE	λ_{\max} =360 nm	0.05 M Na ₂ SO ₄	150 mA/cm ²	—	93 % (4 h)	5.0 % (4 h)			
100 mA/cm ²				—	85 % (4 h)	8.8 % (4 h)				

Table 3 (continued)

Pollutant	Initial concentration (mg/L)	Electrode	Other parameter	Electrolyte	Current/voltage	Fe ²⁺ /Fe ³⁺ (mM)	Pollutant removal	TOC removal	MCE	Reference
			pH=3.0	66.7 mA/cm ²	100 % (8 min)	96 % (6 h)	42 % (max)			
			V=100 mL	100 mA/cm ²	100 % (6 min)	97 % (6 h)	32 % (max)			
Cyanazine	55 110	Anode: Si/BDD (3 cm ²)	Batch O ₂ flow rate—12 mL/min λ_{\max} =360 nm	0.05 M Na ₂ SO ₄	300 mA 100 mA 300 mA	0.5	— — 100 % (35 min)	76 % (3 h) 38 % (3 h) 88 % (3 h)	4.6 % (3 h) 13.8 % (3 h) 10.6 % (3 h)	Borràs et al. 2013
	220 440	Cathode: ADE	pH=3.0 V=100 mL		450 mA 300 mA 300 mA		— — —	89 % (3 h) 67 % (3 h) 55 % (3 h)	7.2 % (3 h) 16.2 % (3 h) 26.6 % (3 h)	
Acid Red 29	244	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch Air flow rate—300 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	33.3 mA/cm ² 66.6 mA/cm ² 100 mA/cm ²	0.5	— — — —	>97 % (3 h) >97 % (3 h)	70 % (max) 50 % (max) 30 % (max)	Almeida et al. 2012
Acid Yellow 36	108	Anode: Si/BDD (20 cm ²) Cathode: ADE	Flow Liquid flow rate—200 L/h λ_{\max} =360 nm pH=3.0 V=2.5 L	0.1 M Na ₂ SO ₄	0.5 A 1 A 2 A 3 A	0.5	— — 100 % (27 min) — —	95 % (6 h) 95 % (5 h) 95 % (4 h) 95 % (3 h)	118 % (max) 100 % (max) 75 % (max) 60 % (max)	Ruiz et al. 2011
Direct Yellow 4	200	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch Air flow rate—0.3 mL/min λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	16.6 mA/cm ² 25 mA/cm ² 33.3 mA/cm ² 66.6 mA/cm ² 100 mA/cm ²	0.5	— — — — —	83 % (6 h) 90 % (4 h) 91 % (4 h) 92 % (4 h) 93 % (4 h)	— — — — —	García-Segura et al. 2012
Sunset Yellow FCF	290	Anode: Si/BDD (3 cm ²) Cathode: ADE	Batch λ_{\max} =360 nm pH=3.0 V=100 mL	0.05 M Na ₂ SO ₄	16.7 mA/cm ² 33.3 mA/cm ² 100 mA/cm ²	0.5	— 100 % (20 min) — —	95 % (2 Ah/L) 95 % (4 Ah/L)	— —	Moreira et al. 2013
2,4-DP	217	Anode: Si/BDD (10 cm ²) Cathode: ADE	Batch O ₂ flow rate—20 mL/min pH=3.0	0.05 M Na ₂ SO ₄	100 mA/cm ² 300 mA/cm ² 450 mA/cm ²	1.0	— 100 % (22 min) —	95 % (7 Ah/L) 83 % (4 h) 93 % (4 h) 98 % (4 h)	— 18 % (4 h) 6.9 % (4 h) 4.8 % (4 h)	Brillas et al. 2007

effect of sunlight and Fe^{2+} had been demonstrated for the complete decolorization and mineralization of anthraquinonic dyes, confirming that SPEF provided a more economical approach for dye treatment (energy consumption of 11.0–26.4 kWh/m³) (Salazar et al. 2012). Taken enrofloxacin of the initial concentration of 158 mg/L as a sample, when the applied current density was 50 mA/cm², the TOC removal ratio by SPEF reached 86 % after 300 min treatment, while only 28 and 45 % by AO and EF, respectively. Moreover, the energy consumption by AO, EF, and SPEF was 0.743, 0.467, and 0.246 kWh/(g TOC), respectively (Guinea et al. 2010). Therefore, this SPEF system seemed to be more attractive for application.

Conclusions and prospect

BDD anode, for its unique and excellent properties, such as good electrochemical stability and high oxygen evolution potential, has attracted more and more attention in the research area of electrochemical oxidation for organic pollutant degradation in recent years. In this review, we illustrated the treatment performance of three kinds of bio-refractory pollutants including pharmaceuticals, pesticides, and synthetic dyes by AO, EF, and PEF systems using BDD as anode. Various works indicated that the performance for pollutants and TOC removal was the best in PEF system, the EF system was inferior, and AO system was the worst. Though electrochemical oxidation has not been widely used for real wastewater treatment mainly due to high cost, it is no doubt that BDD electrode has demonstrated promising prospect in wastewater treatment especially for bio-refractory organic pollutant mineralization. The following aspects were suggested in future research:

1. Though satisfactory removal efficiency can be achieved on the BDD, it still has some unsatisfactory disadvantages, for instance, large area anode fabrication, high cost, and electrode instability during wastewater treatment. So how to improve fabrication process to promote the electrical catalytic performance of BDD electrode in a large scale is still a very key research area. Not like Si or Nb, the material Ti, as a substrate of BDD film, has low cost and high conductivity, so it is a necessity to strengthen the research of Ti/BDD, resolving the problems of cracks and detachment of BDD film. Further, BDD surface modification is supposed to be useful to improve electrocatalytic performance, for example, metallic materials in nanostructure such as nanoparticles of metal (Pt, Ni, Au, Sb) or metal oxide (SnO₂). It was reported that a modified BDD by evenly assembling Sb-doped SnO₂ nanoparticles on the surface was more suitable to degrade pollutants, in which the reaction rate constant of 2,4-D was two times

and mineralization current efficiency at 30 min was 1.6 times than that on the bare BDD (Zhao et al. 2010).

2. As shown in Tables 1, 2, and 3, at present, most of the works have been carried out in batch and in a small scale, which is still far from industrial application. Thus, development scale-up of BDD anode system seems to be very critical, which would make electrochemical oxidation to be a practical technology for wastewater treatment (Zhu et al. 2011). In addition, the total consumption of the process for organic pollutant mineralization is still a little high, so it would be more cost-effective when combined with other wastewater treatment technologies such as biological process.
3. In recent years, a large number of emerging contaminants (e.g., pharmaceuticals and personal care products, endocrine-disrupting compounds, surfactants) enter into the environment not only from industrial activities but also from household activities. The removal of these compounds has become a hot research area in the world. Since the polluted wastewaters containing drugs, pesticides, and dyes can be effectively removed in these three BDD-based systems, it is expected to receive good results for these kinds of compounds. However, how to make this method to be more efficient to meet the real case of low contaminants and low electrolyte concentration in water environment would be a big challenge.

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References

- Almeida LC, Garcia-Segura S, Arias C, Bocchi N, Brillas E (2012) Electrochemical mineralization of the azo dye Acid Red 29 (Chromotrope 2R) by photoelectro-Fenton process. *Chemosphere* 89:751–758
- Aquino JM, Pereira GF, Rocha-Filho RC, Bocchi N, Biaggio SR (2011) Electrochemical degradation of a real textile effluent using boron-doped diamond or $\beta\text{-PbO}_2$ as anode. *J Hazard Mater* 192: 1275–1282
- Balci B, Oturan N, Cherrier R, Oturan MA (2009) Degradation of atrazine in aqueous medium by electrocatalytically generated hydroxyl radicals. A kinetic and mechanistic study. *Water Res* 43: 1924–1934
- Borràs N, Arias C, Oliver R, Brillas E (2011) Mineralization of desmetryne by electrochemical advanced oxidation processes using a boron-doped diamond anode and an oxygen-diffusion cathode. *Chemosphere* 85:1167–1175
- Borràs N, Arias C, Oliver R, Brillas E (2013) Anodic oxidation, electro-Fenton and photoelectro-Fenton degradation of cyanazine using a boron-doped diamond anode and an oxygen-diffusion cathode. *J Electroanal Chem* 689:158–167

- Brillas E, Boye B, Sirés I, Garrido JA, Rodríguez RM, Arias C, Cabot PL, Comninellis C (2004) Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode. *Electrochim Acta* 49: 4487–4496
- Brillas E, Sirés I, Arias C, Cabot PL, Centellas F, Rodríguez RM, Garrido JA (2005) Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode. *Chemosphere* 58:399–406
- Brillas E, Baños MA, Skoumal M, Cabot PL, Garrido JA, Rodríguez RM (2007) Degradation of the herbicide 2,4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using platinum and boron-doped diamond anodes. *Chemosphere* 68:199–209
- Brillas E, Sirés I, Oturan MA (2009) Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chem Rev* 109:6570–6631
- Brillas E, Garcia-Segura S, Skoumal M, Arias C (2010) Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes. *Chemosphere* 79:605–612
- Cavalcanti EB, Garcia-Segura S, Centellas F, Brillas E (2013) Electrochemical incineration of omeprazole in neutral aqueous medium using a platinum or boron-doped diamond anode: degradation kinetics and oxidation products. *Water Res* 47:1803–1815
- Chen GH (2004) Electrochemical technologies in wastewater treatment. *Sep Purif Technol* 38:11–41
- Chen XM, Chen GH (2006) Anodic oxidation of Orange II on Ti/BDD electrode: variable effects. *Sep Purif Technol* 48:45–49
- Chen XM, Chen GH, Lock YP (2003) Anodic oxidation of dyes at novel Ti/B-diamond electrodes. *Chem Eng Sci* 58:995–1001
- Ciríaco L, Anjo C, Correia J, Pacheco MJ, Lopes A (2009) Electrochemical degradation of Ibuprofen on Ti/Pt/PbO₂ and Si/BDD electrodes. *Electrochim Acta* 54:1464–1472
- Costa CR, Montilla F, Morallón E, Olivi P (2009) Electrochemical oxidation of acid black 210 dye on the boron-doped diamond electrode in the presence of phosphate ions: effect of current density, pH, and chloride ions. *Electrochim Acta* 54:7048–7055
- Dirany A, Sirés I, Oturan N, Oturan MA (2010) Electrochemical abatement of the antibiotic sulfamethoxazole from water. *Chemosphere* 81:594–602
- Domínguez JR, González T, Palo P, Sánchez-Martín J (2010) Anodic oxidation of ketoprofen on boron-doped diamond (BDD) electrodes. Role of operative parameters. *Chem Eng J* 162:1012–1018
- El-Ghenymy A, Rodríguez RM, Arias C, Centellas F, Garrido JA, Cabot PL, Brillas E (2013) Electro-Fenton and photoelectro-Fenton degradation of the antimicrobial sulfamethazine using a boron-doped diamond anode and an air-diffusion cathode. *J Electroanal Chem* 701:7–13
- Flox C, Cabot PL, Centellas F, Garrido JA, Rodríguez RM, Arias C, Brillas E (2006) Electrochemical combustion of herbicide mecoprop in aqueous medium using a flow reactor with a boron-doped diamond anode. *Chemosphere* 64:892–902
- Frontistis Z, Brebou C, Venieri D, Mantzavinos D, Katsaounis A (2011) BDD anodic oxidation as tertiary wastewater treatment for the removal of emerging micro-pollutants, pathogens and organic matter. *J Chem Technol Biotechnol* 86:1233–1236
- Garcia-Segura S, El-Ghenymy A, Centellas F, Rodríguez RM, Arias C, Garrido JA, Cabot PL, Brillas E (2012) Comparative degradation of the diazo dye Direct Yellow 4 by electro-Fenton, photoelectro-Fenton and photo-assisted electro-Fenton. *J Electroanal Chem* 681:36–43
- Guinea E, Garrido JA, Rodríguez RM, Cabot PL, Arias C, Centellas F, Brillas E (2010) Degradation of the fluoroquinolone enrofloxacin by electrochemical advanced oxidation processes based on hydrogen peroxide electrogeneration. *Electrochim Acta* 55:2101–2115
- Hamza M, Abdelhedi R, Brillas E, Sirés I (2009) Comparative electrochemical degradation of the triphenylmethane dye Methyl Violet with boron-doped diamond and Pt anodes. *J Electroanal Chem* 627: 41–50
- Irmak S, Yavuz HI, Erbatur O (2006) Degradation of 4-chloro-2-methylphenol in aqueous solution by electro-Fenton and photoelectro-Fenton processes. *Appl Catal B Environ* 63:243–248
- Isarain-Chávez E, Rodríguez RM, Garrido JA, Arias C, Centellas F, Cabot PL, Brillas E (2010) Degradation of the beta-blocker propranolol by electrochemical advanced oxidation processes based on Fenton's reaction chemistry using a boron-doped diamond anode. *Electrochim Acta* 56:215–221
- Liu L, Zhao GH, Wu MF, Lei YZ, Rong G (2009) Electrochemical degradation of chlorobenzene on boron-doped diamond and platinum electrodes. *J Hazard Mater* 168:179–186
- Luong JHT, Male KB, Glennon JD (2009) Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications. *Analyst* 134:1965–1979
- Martínez-Huitle CA, Brillas E (2009) Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. *Appl Catal B Environ* 87:105–145
- Migliorini FL, Braga NA, Alves SA, Ferreira NG (2011) Anodic oxidation of wastewater containing the Reactive Orange 16 Dye using heavily boron-doped diamond electrodes. *J Hazard Mater* 192: 1683–1689
- Montanaro D, Petrucci E (2009) Electrochemical treatment of Remazol Brilliant Blue on a boron-doped diamond electrode. *Chem Eng J* 153:138–144
- Moreira FC, Garcia-Segura S, Vilar VJP, Boaventura RAR, Brillas E (2013) Decolorization and mineralization of Sunset Yellow FCF azo dye by anodic oxidation, electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton processes. *Appl Catal B Environ* 142–143:877–890
- Muruganathan M, Yoshihara S, Rakuma T, Uehara N, Shirakashi T (2007) Electrochemical degradation of 17 β -estradiol (E2) at boron-doped diamond (Si/BDD) thin film electrode. *Electrochim Acta* 52:3242–3249
- Muruganathan M, Yoshihara S, Rakuma T, Shirakashi T (2008) Mineralization of bisphenol A (BPA) by anodic oxidation with boron-doped diamond (BDD) electrode. *J Hazard Mater* 154: 213–220
- Muruganathan M, Latha SS, Bhaskar RG, Yoshihara S (2011) Role of electrolyte on anodic mineralization of atenolol at boron doped diamond and Pt electrodes. *Sep Purif Technol* 79:56–62
- Oturan N, Hamza M, Ammar S, Abdelhédi R, Oturan MA (2011) Oxidation/mineralization of 2-nitrophenol in aqueous medium by electrochemical advanced oxidation processes using Pt/carbon-felt and BDD/carbon-felt cells. *J Electroanal Chem* 661:66–71
- Özcan A, Savas-Koparal A, Oturan MA (2008) Protham mineralization in aqueous medium by anodic oxidation using boron-doped diamond anode: influence of experimental parameters on degradation kinetics and mineralization efficiency. *Water Res* 42: 2889–2898
- Panizza M, Cerisola G (2005) Application of diamond electrodes to electrochemical processes. *Electrochim Acta* 51:191–199
- Panizza M, Cerisola G (2009) Direct and mediated anodic oxidation of organic pollutants. *Chem Rev* 109:6541–6569
- Pecková K, Musilová J, Barek J (2009) Boron-doped diamond film electrodes—new tool for voltammetric determination of organic substances. *Crit Rev Anal Chem* 39:148–172
- Petrucci E, Montanaro D (2011) Anodic oxidation of a simulated effluent containing Reactive Blue 19 on a boron-doped diamond electrode. *Chem Eng J* 174:612–618
- Quiroz Alfaro MA, Ferro S, Martínez-Huitle CA, Meas Y (2006) Boron doped diamond electrode for the wastewater treatment. *J Braz Chem Soc* 17:227–231

- Reis RM, Baio JAF, Migliorini FL, Rocha RS (2013) Degradation of dipyrone in an electrochemical flow-by reactor using anodes of boron-doped diamond (BDD) supported on titanium. *J Electroanal Chem* 690:89–95
- Ruiz EJ, Arias C, Brillas E, Hernández-Ramírez A, Peralta-Hernández JM (2011) Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photoelectro-Fenton processes with a boron-doped diamond anode. *Chemosphere* 82:495–501
- Salazar R, Brillas E, Sirés I (2012) Finding the best $\text{Fe}^{2+}/\text{Cu}^{2+}$ combination for the solar photoelectro-Fenton treatment of simulated wastewater containing the industrial textile dye Disperse Blue 3. *Appl Catal B Environ* 115–116:107–116
- Samet Y, Agengui L, Abdelhédi R (2010) Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes. *Chem Eng J* 161:167–172
- Sirés I, Brillas E (2012) Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: a review. *Environ Int* 40:212–229
- Sirés I, Cabot PL, Centellas F, Garrido JA, Rodríguez RM, Arias C, Brillas E (2006) Electrochemical degradation of clofibrac acid in water by anodic oxidation. Comparative study with platinum and boron-doped diamond electrodes. *Electrochim Acta* 52:75–85
- Sirés I, Garrido JA, Rodríguez RM, Brillas E, Oturan N, Oturan MA (2007a) Catalytic behavior of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system in the electro-Fenton degradation of the antimicrobial chlorophene. *Appl Catal B Environ* 72:382–394
- Sirés I, Oturan N, Oturan MA, Rodríguez RM, Garrido JA, Brillas E (2007b) Electro-Fenton degradation of antimicrobials triclosan and triclocarban. *Electrochim Acta* 52:5493–5503
- Skoumal M, Arias C, Cabot PL, Centellas F, Garrido JA, Rodríguez RM, Brillas E (2008) Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes. *Chemosphere* 71:1718–1729
- Sun JR, Lu HY, Du LL, Lin HB, Li HD (2011) Anodic oxidation of anthraquinone dye Alizarin Red S at Ti/BDD electrodes. *Appl Surf Sci* 257:6667–6671
- Sun JR, Lu HY, Lin HB, Du LL, Huang WM, Li HD, Cui T (2012) Electrochemical oxidation of aqueous phenol at low concentration using Ti/BDD electrode. *Sep Purif Technol* 88:116–120
- Wu MF, Zhao GH, Li MF, Liu L, Li DM (2009) Applicability of boron-doped diamond electrode to the degradation of chloride-mediated and chloride-free wastewaters. *J Hazard Mater* 163:26–31
- Zhang C, Jiang YH, Li YL, Hu ZX, Zhou L, Zhou MH (2013) Three-dimensional electrochemical process for wastewater treatment: a general review. *Chem Eng J* 228:455–467
- Zhao G, Li P, Nong F, Li M, Gao J, Li D (2010) Construction and high performance of a novel modified boron-doped diamond film electrode endowed with superior electrocatalysis. *J Phys Chem C* 114:5906–5913
- Zhou MH, Särkkä H, Sillanpää M (2011) A comparative experimental study on methyl orange degradation by electrochemical oxidation on BDD and MMO electrodes. *Sep Purif Technol* 78:290–297
- Zhou L, Hu ZX, Zhang C, Bi ZH, Jin T, Zhou MH (2013) Electro-generation of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode. *Sep Purif Technol* 111:131–136
- Zhu XP, Ni JR, Lai P (2009) Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes. *Water Res* 43:4347–4355
- Zhu XP, Ni JR, Wei JJ, Chen P (2011) Scale-up of B-doped diamond anode system for electrochemical oxidation of phenol simulated wastewater in batch mode. *Electrochim Acta* 56:9439–9447