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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.

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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 (·OH) which has so high standard redox potential (E^0(·OH/H_2O)=2.80 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).

Generally, an ideal anode for pollutant degradation must have high O_2 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, IrO_2, RuO_2, SnO_2, and PbO_2 (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 CH_4 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 B_2H_6 or $B(OCH_3)_3$ 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 (·OH) (Panizza and Cerisola 2009; Moreira et al. 2013). When BDD is used, hydroxyl radical BDD(·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).

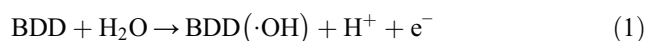$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \qquad (1)$$

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 H_2O_2 through the electrochemical reduction of O_2. This process is called AO-H_2O_2 which also belongs to the scope of anodic oxidation. As to the supporting electrolyte, Na_2SO_4 is usually selected for the following reasons: (1) relatively cheap, (2) it could be oxidized into $S_2O_8^{2-}$ which also participated in the degradation of organics, and (3) it would not produce hazardous compounds during treatment; the presence of Na_2SO_4 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/cm^2), 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/cm^2, respectively (Muruganantham 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	0.1 M Na$_2$SO$_4$	12.5 mA/cm^2 25 mA/cm^2	100 % (40 min) 100 % (40 min)	58 % (4.5 h) 80 % (4.5 h)	2.04–1.13 % –	Murugananthan et al. 2007
			V=500 mL		50 mA/cm^2	100 % (30 min)	94 % (4.5 h)	1.02–0.874 %	
Atenolol	2.25 µM	Anode: Si/BDD (11.25 cm^2)	Batch	0.1 M Na$_2$SO$_4$	4.44 mA/cm^2	–	80 % (25 h)	–	Murugananthan et al. 2011
		Cathode: Pt	pH=6.0		8.88 mA/cm^2	–	96 % (25 h)	–	
			V=250 mL		13.3 mA/cm^2	–	100 % (20 h)	–	
Chloroxylenol	100 mg/L	Anode: Si/BDD (3 cm^2) Cathode: stainless steel	Batch pH=3.0	0.05 M Na$_2$SO$_4$	33 mA/cm^2 100 mA/cm^2	100 % (420 min) 100 % (240 min)	>96 % (5 h) >96 % (5 h)	14 % (3 h) 5.5 % (3 h)	Skoumal et al. 2008
			V=100 mL		150 mA/cm^2	100 % (180 min)	>96 % (5 h)	4.0 % (3 h)	
Bisphenol A	20 mg/L	Anode: Si/BDD (7 cm^2) Cathode: Pt	Batch pH=6.0	0.1 M Na$_2$SO$_4$	14.28 mA/cm^2 25 mA/cm^2	100 % (10 h) 100 % (9 h)	100 % (24 h) 100 % (16 h)	3.4 % –	Murugananthan et al. 2008
			V=250 mL		35.7 mA/cm^2	100 % (5 h)	100 % (14 h)	2.65 %	
Clofibric acid	179 mg/L	Anode: Si/BDD (3 cm^2) Cathode: stainless steel	Batch pH=12	0.05 M Na$_2$SO$_4$	33 mA/cm^2 100 mA/cm^2	100 % (540 min) 100 % (420 min)	100 % (10 Ah/L) 100 % (21 Ah/L)	– –	Sirés et al. 2006
			V=100 mL		150 mA/cm^2	100 % (360 min)	100 % (27 Ah/L)	–	
Diclofenac	175 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=6.5	0.05 M Na$_2$SO$_4$	50 mA/cm^2 100 mA/cm^2	93.1 % (360 min) 98.9 % (360 min)	78 % (6 h) 85 % (6 h)	– –	Brillas et al. 2010
		Cathode: stainless steel	V=100 mL		300 mA/cm^2	100 % (300 min)	97 % (6 h)	–	
					450 mA/cm^2	100 % (200 min)	99 % (6 h)	–	
Dipyrone	100 mg/L	Anode: Ti/BDD (14.4 cm^2)	Flow, flow rate—50 L/h	0.1 M H$_2$SO$_4$	3.5 V 4.0 V	100 % (120 min) 100 % (90 min)	8 % 15 %	– –	Reis et al. 2013
		Cathode: DSA	V=2.0 L	0.1 M K$_2$SO$_4$	4.5 V 5.0 V	100 % (45 min) 100 % (25 min)	30 % 44 %	– –	
Enrofloxacin	158 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	0.05 M Na$_2$SO$_4$	33 mA/cm^2	78 % (360 min)	>97 % (6 h)	–	Guinea et al. 2010
		Cathode: ADE	V=100 mL						
Ibuprofen	1.75 mM	Anode: Si/BDD (20 cm^2)	Batch	0.035 M Na$_2$SO$_4$	10 mA/cm^2	–	85 % (6 h)	–	Ciríaco et al. 2009
		Cathode: stainless steel foils			20 mA/cm^2	–	90 % (6 h)	–	
					30 mA/cm^2	–	95 % (6 h)	–	
Omeprazole	169 mg/L	Anode: Si/BDD (3 cm^2) Cathode: ADE	Batch pH=7.0	0.05 M Na$_2$SO$_4$	33.3 mA/cm^2 66.6 mA/cm^2	100 % (75 min) 100 % (80 min)	45 % (6 h) 54 % (6 h)	10 % (6 h) 6.0 % (6 h)	Cavalcanti et al. 2013
			V=100 mL		100 mA/cm^2	100 % (150 min)	78 % (6 h)	5.8 % (6 h)	
Paracetamol	157 mg/L	Anode: Si/BDD (3 cm^2) Cathode: graphite	Batch pH=3.0	0.05 M Na$_2$SO$_4$	100 mA/cm^2 300 mA/cm^2	– 100 % (150 min)	64 % (4 h) 91 % (4 h)	15 % (4 h) 7.2 % (4 h)	Brillas et al. 2005
			V=100 mL		450 mA/cm^2	–	98 % (4 h)	5.2 % (4 h)	
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
			V=100 mL		166.7 mA/cm^2	–	70 % (3 h)	4.6 % (3 h)	
MCPA					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)	
					166.7 mA/cm^2	–	66 % (3 h)	6.6 % (3 h)	
2,4-D					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)	
					166.7 mA/cm^2	–	94 % (3 h)	5.8 % (3 h)	
2,4,5-T					33.3 mA/cm^2	100 % (360 min)	59 % (3 h)	15 % (3 h)	
					100 mA/cm^2				
					166.7 mA/cm^2	–	77 % (3 h)	6.7 % (3 h)	
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$_4$	100 mA/cm^2 300 mA/cm^2 450 mA/cm^2	100 % (300 min) – –	63 % (4 h) 82 % (4 h) 97 % (4 h)	14 % 6.1 % 4.8 %	Brillas et al. 2007
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$_4$	100 mA 300 mA 450 mA 300 mA	– 100 % (80 min) – –	27 % (3 h) 60 % (3 h) 68 % (3 h) 51 % (3 h)	9.9 % 7.3 % 5.5 % 12.3 %	Borràs et al. 2011
	220 mg/ 440 mg/L				300 mA	–	49 % (3 h)	23.7 %	
Mecoprop	178 mg/L	Anode: Si/BDD (20 cm^2) Cathode: stainless steel	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 mA/cm^2 150 mA/cm^2	100 % (15 min) 100 % (15 min) 100 % (17 min)	100 % (14 Ah/L) 100 % (18 Ah/L) 100 % (27 Ah/L)	– – –	Flox et al. 2006
Propham	0.5 mM	Anode: Nb/BDD	Batch	0.05 M Na$_2$SO$_4$	30 mA 50 mA	100 % (180 min) 100 % (180 min)	62 % (3 h) 77 % (3 h)	77.68 % (180 min) 58.44 % (180 min)	Özcan et al. 2008
			pH=3.0		100 mA	100 % (180 min)	84 % (3 h)	31.72 % (180 min)	
					300 mA	100 % (180 min)	94 % (3 h)	11.92 % (180 min)	
		Cathode: Pt gauze			500 mA	100 % (180 min)	95 % (3 h)	7.2 % (180 min)	
			V=0.15 L	0.1 M NaNO$_3$	100 mA	100 % (180 min)	43 % (3 h)	16.22 % (180 min)	
				0.1 M LiClO$_4$	100 mA	100 % (180 min)	82 % (3 h)	31.08 % (180 min)	
				0.1 M NaCl	100 mA	100 % (15 min)	69 % (3 h)	26.16 % (180 min)	
Cyanazine	55 mg/L 110 mg/L	Anode: Si/BDD (3 cm^2) Cathode: ADE	Batch pH=3.0 V=100 mL	0.05 M Na$_2$SO$_4$	100 mA/cm^2 33.3 mA/cm^2 100 mA/cm^2 150 mA/cm^2	– – 91 % (60 min) –	68 % (4 h) 37 % (4 h) 66 % (4 h) 69 % (4 h)	2.8 % (4 h) 8.9 % (4 h) 5.2 % (4 h) 3.7 % (4 h)	Borràs et al. 2013
	145 mg/L				100 mA/cm^2	–	59 % (4 h)	6.1 % (4 h)	
Acid black 210	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	25 mA/cm^2 50 mA/cm^2	– –	51 % (3 h) 74 % (3 h)	– –	Costa et al. 2009

Table 1 (continued)

Pollutant	Initial concentration	Electrode	Other parameters	Electrolyte	Current/voltage	Pollutant removal	TOC removal	MCE	Reference
			V=250 mL		100 mA/cm^2	–	100 % (3 h)	–	
Methyl orange	50 mg/L	Anode: Si/BDD (3 cm^2) Cathode: stainless steel	Batch pH=3.0	0.1 M Na$_2$SO$_4$ 0.1 M Na$_2$SO$_4$ & 0.05 M NaCl	50 mA/cm^2	– –	25 % 56 %	– –	Zhou et al. 2011
			V=200 mL						
Methyl violet	200 mg/L (TOC)	Anode: Si/BDD (3 cm^2) Cathode: stainless steel	Batch pH=3.0	0.05 M Na$_2$SO$_4$	33.3 mA/cm^2 100 mA/cm^2	49 % (600 min) 92 % (600 min)	56 % (4 h) 83 % (4 h)	42 % (max) 27 % (max)	Hamza et al. 2009
			V=100 mL		150 mA/cm^2	97 % (600 min)	90 % (4 h)	17 % (max)	
Orange II	750 mg/L	Anode: Ti/BDD	Flow	2 g/L Na$_2$SO$_4$	100 A/m^2 200 A/m^2	– –	97 % (COD) 92 % (COD)	58.3 % 54.9 %	Chen and Chen 2006
					400 A/m^2	–	84 % (COD)	50.7 %	
		Cathode: stainless steel	Batch pH=8.5	1.5 g/L Na$_2$SO$_4$	100 A/m^2 200 A/m^2	– –	82 % (COD) 91 % (COD)	– –	
			V=35 mL		400 A/m^2	–	98 % (COD)	–	
Reactive Orange 16	85 mg/L	Anode: Si/BDD (1.44 cm^2)	Flow, flow rate—7 L/min pH=5.6	0.1 M Na$_2$SO$_4$	10 mA/cm^2 30 mA/cm^2	60 % (0.25 Ah/L) 100 % (0.20 Ah/L)	– –	– –	Migliorini et al. 2011
		Cathode: Pt foil (2 cm^2)	V=300 mL	0.05 M NaCl	50 mA/cm^2 70 mA/cm^2	100 % (0.10 Ah/L) 100 % (0.06 Ah/L)	– –	– –	
Reactive Blue 19	50 mg/L	Anode: Ti/BDD (5 cm^2)	Batch	0.023 M Na$_2$SO$_4$	200 A/m^2	100 % (90 min)	75 % (410 min)	–	Petrucci and Montanaro 2011
		Cathode: Pt wire		0.01 M Na$_2$CO$_3$	300 A/m^2 600 A/m^2	100 % (60 min) 100 % (30 min)	75 % (370 min) 75 % (260 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	200 A/m^2 300 A/m^2	100 % (10 min) 100 % (8 min)	45 % (160 min) 70 % (160 min)	– –	Montanaro and Petrucci 2009
			V=100 mL		400 A/m^2	100 % (7 min)	100 % (160 min)	–	
Sunset Yellow FCF	290 mg/L	Anode: Si/BDD (3 cm^2) Cathode: ADE	Batch pH=3.0	0.05 M Na$_2$SO$_4$	16.7 mA/cm^2 33.3 mA/cm^2	– 95 % (360 min)	45 % (3 Ah/L) 70 % (3 Ah/L)	– –	Moreira et al. 2013
			V=100 mL		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/cm^2, 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,

$$\text{MCE} \ (\%) \ = \ \frac{nFV\Delta \ (\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \ mIt} \times 100 \qquad (2)$$
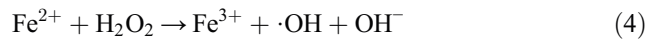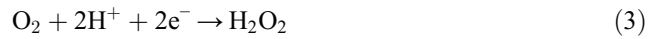
where F is the Faraday constant (96,485 C/mol), V is the solution volume (L), $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC removal, 4.32×10^7 is a conversion factor (3,600 s/h × 12,000 mg/mol), m is the number of carbon atoms of the pollutant, I is the applied current (A), t is the electrolysis 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/cm^2 (Borràs et al. 2013). This phenomenon can be explained by the acceleration of generating other weak oxidants such as $S_2O_8^{2-}$ ($2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$) 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 $\cdot OH$ 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 $\cdot O_2^-$ radical ($E^0 = -0.33$ V/NHE) in cathode compartment (Eq. 6) (Irmak et al. 2006).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad (4)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (5)$$

$$O_2 + e^- \rightarrow \cdot O_2^- \qquad (6)$$

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, $\cdot OH$ is formed in two different ways: One is produced on the surface of BDD, and the other is formed via electro-Fenton reaction (Oturan et al. 2011). As a result, the generation rate of $\cdot OH$ 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/cm^2, respectively (Sirés et Al. 2007a). The improvement of removal efficiency with current density was attributed to the production of higher amounts of $\cdot OH$ 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)	Batch pH=3.0	0.05 M Na$_2$SO$_4$	3.3 mA/cm^2	0.5	–	68 % (DOC, 6 h)	–	Ciríaco et al. 2009
					13.3 mA/cm^2		–	92 % (DOC, 6 h)	–	
		Cathode: ADE	O$_2$ flow rate—20 mL/min V=100 mL		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	0.05 M Na$_2$SO$_4$	33 mA/cm^2	0.1	–	59 % (4 h)	–	Guinea et al. 2010
						0.2	–	64 % (4 h)	–	
			V=100 mL			0.5	–	67 % (4 h)	–	
Chlorophene	84 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	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)	
		Cathode: ADE	O$_2$ flow rate—20 mL/min		200 mA/cm^2		–	85 % (11 h)	12 % (60 min)	
			V=200 mL		300 mA/cm^2		100 % (90 min)	97 % (11 h)	10 % (60 min)	
Chloroxylenol	100 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	0.05 M Na$_2$SO$_4$	33 mA/cm^2	1.0	100 % (20 min)	82 %	24 % (max)	Skoumal et al. 2008
		Cathode: ADE	O$_2$ flow rate—20 mL/min V=100 mL							
Atenolol	158 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	0.05 M Na$_2$SO$_4$	50 mA	0.5	88 % (60 min)	77 % (360 min)	18–50 % (360 min)	Murugananthan et al. 2011
		Cathode: ADE	O$_2$ flow rate—20 mL/min V=100 mL							
Propranolol	154 mg/L	Anode: Si/BDD (3 cm^2)	Batch	0.05 M Na$_2$SO$_4$	10 mA/cm^2	0.5	–	78 % (420 min)	75 % (max)	Isarain-Chávez et al. 2010
			pH=3.0		20 mA/cm^2		–	80 % (420 min)	47 % (max)	
		Cathode: ADE	O$_2$ flow rate—20 mL/min		40 mA/cm^2		100 % (29 min)	85 % (420 min)	24 % (max)	
			V=100 mL		60 mA/cm^2		–	88 % (420 min)	16 % (max)	
					80 mA/cm^2		–	91 % (420 min)	11 % (max)	
Sulfamethazine	193 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	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)	–	
		Cathode: ADE	Air flow rate—300 mL/min V=100 mL		100 mA/cm^2		100 % (5 min)	94 % (DOC, 420 min)	–	
Sulfamethoxazole	0.208 mM	Anode: Nb/BDD (25 cm^2)	Batch pH=3.0	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)	–	
		Cathode: carbon felt	Air flow rate—1.0 L/min		100 mA		100 % (20 min)	94 % (600 min)	–	
			V=220 mL		200 mA		100 % (15 min)	96 % (600 min)	–	
					300 mA		100 % (15 min)	98 % (600 min)	–	
Triclosan	50 mg/L	Anode: Si/BDD (3 cm^2)	Batch pH=3.0	0.05 M Na$_2$SO$_4$	60 mA	0.2	100 % (120 min)	–	–	Sirés et al. 2007b
		Cathode: ADE	O$_2$ flow rate—12 mL/min		300 mA		100 % (90 min)	–	–	
Triclocarban	5 mg/L		V=200 mL		60 mA		100 % (120 min)	–	–	
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
		Cathode: carbon felt	Air flow rate—1 L/min				–	72 % (5 h)	–	
			$V=150$ mL				–	82 % (10 h)	–	
2,4-DP	217 mg/L	Anode: Si/BDD (10 cm^2)	Batch O$_2$ flow rate—20 mL/min	0.05 M Na$_2$SO$_4$	100 mA/cm^2	1.0	100 % (25 min)	82 % (4 h)	18 % (4 h)	Brillas et al. 2007
		Cathode: ADE	pH=3.0		300 mA/cm^2		–	88 % (4 h)	6.6 % (4 h)	
			$V=100$ mL		450 mA/cm^2		–	97 % (4 h)	4.7 % (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) 47 % (240 min)	3.5 % (4 h) 11.3 % (4 h)	Borràs et al. 2013
		Cathode: ADE	O$_2$ flow rate—20 mL/min		100 mA/cm^2		95 % (60 min)	82 % (240 min)	6.6 % (4 h)	
			$V=100$ mL		150 mA/cm^2		–	87 % (240 min)	4.7 % (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) 36 % (3 h)	4.1 % (3 h) 13.1 % (3 h)	Borràs et al. 2011
					300 mA		100 % (45 min)	78 % (3 h)	9.5 % (3 h)	
		Cathode: ADE	pH=3.0		450 mA		–	88 % (3 h)	7.1 % (3 h)	
	220 mg/L		$V=100$ mL		300 mA		–	63 % (3 h)	15.2 % (3 h)	
	440 mg/L				300 mA		–	55 % (3 h)	26.6 % (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 % 98.7 %	– –	– –	Ruiz et al. 2011
		Cathode: Si/BDD	Air flow rate—1 L/min $V=100$ mL		23 mA/cm^2		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	– 100 % (27 min)	46 % (360 min) 54 % (360 min)	56 % (max) 45 % (max)	
		Cathode: ADE	Liquid flow rate—200 L/h		2 A		–	61 % (360 min)	32 % (max)	
			$V=2.5$ L		3 A		–	71 % (360 min)	30 % (max)	
	40 mg/L	Anode: Si/BDD (0.785 cm^2)	Batch	–	Anodic potential—2.5 v	1	94 % (180 min)	–	–	
						6	69 % (180 min)	–	–	
		Cathode: Pt wire				8	69 % (180 min)	–	–	
						12	58 % (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) 74 % (240 min)	– –	Garcia-Segura et al. 2012
		Cathode: ADE	Air flow rate—0.3 mL/min		66.6 mA/cm^2		–	85 % (240 min)	–	
			$V=100$ mL		100 mA/cm^2		–	83 % (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) 80 % (3 h)	22 % (3 h) 7.9 % (3 h)	Brillas et al. 2004
			O$_2$ flow rate—20 mL/min		166.7 mA/cm^2		–	87 % (3 h)	5.7 % (3 h)	
MCPA					33.3 mA/cm^2		100 % (30 min)	76 % (3 h)	24 % (3 h)	
			pH=3.0		100 mA/cm^2		–	87 % (3 h)	9.1 % (3 h)	
		Cathode: ADE			166.7 mA/cm^2		–	90 % (3 h)	6.3 % (3 h)	
2,4-D					33.3 mA/cm^2		100 % (12 min)	78 % (3 h)	22 % (3 h)	

$$2BDD(\cdot OH) \rightarrow 2BDD + O_2 + 2H^+ + 2e^- \qquad (7)$$

$$2\cdot OH \rightarrow H_2O_2 \qquad (8)$$

$$H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \qquad (9)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad (10)$$

$$2SO_4{}^{2-} \rightarrow S_2O_8{}^{2-} + 2e^- \qquad (11)$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^- \qquad (12)$$

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/cm^2. 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/cm^2, 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

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		–	90 % (3 h)	8.4 % (3 h)	Moreira et al. 2013
					166.7 mA/cm^2		–	99 % (3 h)	6.1 % (3 h)	
					33.3 mA/cm^2		100 % (10 min)	80 % (3 h)	21 % (3 h)	
					100 mA/cm^2		–	89 % (3 h)	7.7 % (3 h)	
					166.7 mA/cm^2		–	97 % (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 NaSO$_4$	16.7 mA/cm^2	0.5	–	75 % (3 Ah/L)	–	
					33.3 mA/cm^2		100 % (26 min)	85 % (6 Ah/L)	–	
					100 mA/cm^2		–	90 % (18 Ah/L)	–	

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 $Fe(OH)^{2+}$, 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 $\cdot OH$ via reaction (13) (Ruiz et al. 2011):

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \cdot OH \qquad (13)$$
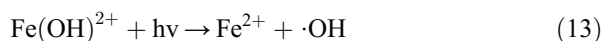
2. The quick photolysis of Fe(III)–carboxylate complexes, taken oxalic acid as example; the forms of Fe(III)–carboxylate complexes are $Fe(C_2O_4)^+$, $Fe(C_2O_4)_2^-$, and $Fe(C_2O_4)_3^{3-}$, and these complexes can be mineralized according to reaction (14) under irradiation (Ciríaco et al. 2009):

$$2\,Fe(C_2O_4)_n^{3-2n} + hv \rightarrow 2Fe^{2+} + (2n-1)\,C_2O_4^{2-} + 2CO_2 \qquad (14)$$
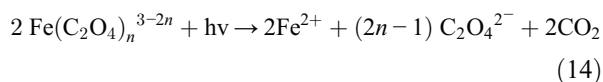
Figure 1 shows a general degradation pathway of aromatic organic pollutants by AO, EF, or PEF process (Brillas et al. 2004; Murugananthan et al. 2008). The target pollutant was firstly attacked by BDD($\cdot$OH) and $\cdot$OH, and as a result, it was degraded into some aromatic derivatives and further 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 $\cdot$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 $\cdot$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
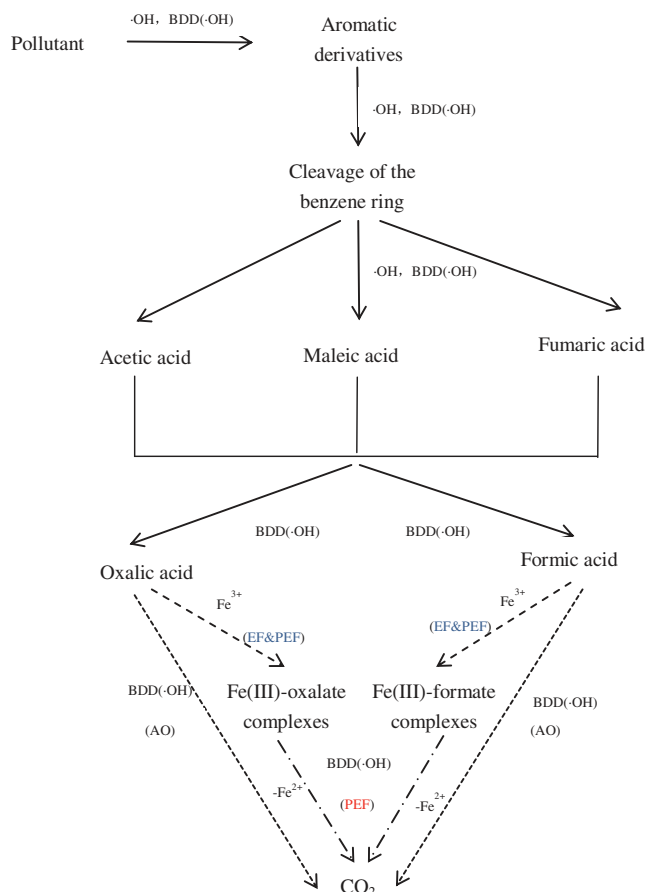

Fig. 1 A general pathway for aromatic pollutant degradation by AO, EF, and PEF

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 ($\lambda_{max}=360$ nm) was placed at the top of the open cell, supplying a photoionization energy input of 140 $\mu W/cm^2$ 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 mA/cm². 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 mA/cm². In addition, when the current density was 100 mA/cm², 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)	
					100 mA/cm^2		–	59 % (1.5 h)	–	
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)	
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 % (10 min)	86 % (6 h)	71 % (max)	El-Ghenymy et al. 2013
					66.7 mA/cm^2		100 % (8 min)	96 % (6 h)	42 % (max)	
					100 mA/cm^2		100 % (6 min)	97 % (6 h)	32 % (max)	
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 Cathode: ADE λ_{max}=360 nm	0.05 M Na$_2$SO$_4$	100 mA/cm^2	0.5	–	91 % (4 h)	3.7 % (4 h)	Borràs et al. 2013
	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)	
					150 mA/cm^2		–	93 % (4 h)	5.0 % (4 h)	
	145				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	Anode: Si/BDD (3 cm^2)	Batch	0.05 M Na$_2$SO$_4$	300 mA	0.5	–	76 % (3 h)	4.6 % (3 h)	Borràs et al. 2013
	110		O$_2$ flow rate—12 mL/min		100 mA			38 % (3 h)	13.8 % (3 h)	
			λ$_{max}$=360 nm		300 mA		100 % (35 min)	88 % (3 h)	10.6 % (3 h)	
		Cathode: ADE	pH=3.0		450 mA		–	89 % (3 h)	7.2 % (3 h)	
	220		V=100 mL		300 mA		–	67 % (3 h)	16.2 % (3 h)	
	440				300 mA			55 % (3 h)	26.6 % (3 h)	
Acid Red 29	244	Anode: Si/BDD (3 cm^2)	Batch Air flow rate—300 mL/min	0.05 M Na$_2$SO$_4$	33.3 mA/cm^2	0.5	–	>97 % (3 h)	70 % (max)	Almeida et al. 2012
		Cathode: ADE	λ$_{max}$=360 nm							
			pH=3.0		66.6 mA/cm^2		–	>97 % (3 h)	50 % (max)	
			V=100 mL		100 mA/cm^2		–	>97 % (3 h)	30 % (max)	
Acid Yellow 36	108	Anode: Si/BDD (20 cm^2)	Flow Liquid flow rate—200 L/h	0.1 M Na$_2$SO$_4$	0.5 A	0.5	–	95 % (6 h)	118 % (max)	Ruiz et al. 2011
		Cathode: ADE	λ$_{max}$=360 nm		1 A		100 % (27 min)	95 % (5 h)	100 % (max)	
			pH=3.0		2 A		–	95 % (4 h)	75 % (max)	
			V=2.5 L		3 A		–	95 % (3 h)	60 % (max)	
Direct Yellow 4	200	Anode: Si/BDD (3 cm^2)	Batch Air flow rate—0.3 mL/min	0.05 M Na$_2$SO$_4$	16.6 mA/cm^2	0.5	–	83 % (6 h)	–	Garcia-Segura et al. 2012
					25 mA/cm^2		–	90 % (4 h)	–	
		Cathode: ADE	λ$_{max}$=360 nm		33.3 mA/cm^2			91 % (4 h)	–	
			pH=3.0		66.6 mA/cm^2			92 % (4 h)	–	
			V=100 mL		100 mA/cm^2			93 % (4 h)	–	
Sunset Yellow FCF	290	Anode: Si/BDD (3 cm^2) Cathode: ADE	Batch λ$_{max}$=360 nm pH=3.0	0.05 M Na$_2$SO$_4$	16.7 mA/cm^2	0.5	–	95 % (2 Ah/L)	–	Moreira et al. 2013
					33.3 mA/cm^2		100 % (20 min)	95 % (4 Ah/L)	–	
			V=100 mL		100 mA/cm^2		–	95 % (7 Ah/L)	–	
2,4-DP	217	Anode: Si/BDD (10 cm^2)	Batch	0.05 M Na$_2$SO$_4$	100 mA/cm^2	1.0	100 % (22 min)	83 % (4 h)	18 % (4 h)	Brillas et al. 2007
		Cathode: ADE	O$_2$ flow rate—20 mL/min		300 mA/cm^2		–	93 % (4 h)	6.9 % (4 h)	
			pH=3.0		450 mA/cm^2		–	98 % (4 h)	4.8 % (4 h)	

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/m^3) (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/cm^2, 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 (SnO_2). It was reported that a modified BDD by evenly assembling Sb-doped SnO_2 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 BBD-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.

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 β-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/PbO$_2$ 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 JÁ, 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

Murugananthan M, Yoshihara S, Rakuma T, Uehara N, Shirakashi T (2007) Electrochemical degradation of 17β-estradiol (E2) at boron-doped diamond (Si/BDD) thin film electrode. Electrochim Acta 52:3242–3249

Murugananthan 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

Murugananthan 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) Propham 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 Fe^{2+}/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, Rodriguez RM, Arias C, Brillas E (2006) Electrochemical degradation of clofibric 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 Fe^{3+}/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