#### **REVIEW ARTICLE**

# Recent electrochemical methods in electrochemical degradation of halogenated organics: a review



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#### Abstract

Halogenated organics are widely used in modern industry, agriculture, and medicine, and their large-scale emissions have led to soil and water pollution. Electrochemical methods are attractive and promising techniques for wastewater treatment and have been developed for degradation of halogenated organic pollutants under mild conditions. Electrochemical techniques are classified according to main reaction pathways: (i) electrochemical reduction, in which cleavage of C-X (X = F, Cl, Br, I) bonds to release halide ions and produce non-halogenated and non-toxic organics and (ii) electrochemical oxidation, in which halogenated organics are degraded by electrogenerated oxidants. The electrode material is crucial to the degradation efficiency of an electrochemical process. Much research has therefore been devoted to developing appropriate electrode materials for practical applications. This paper reviews recent developments in electrode materials for electrochemical degradation of halogenated organics. And at the end of this paper, the characteristics of new combination methods, such as photocatalysis, nanofiltration, and the use of biochemical method, are discussed.

**Keywords** Halogenated organics · Electrochemical reduction · Electrochemical oxidation · Combined techniques · Photoelectrochemistry · Electrode materials

## Introduction

In recent decades, with the rapid development of society and economies, the problem of environmental pollution has become increasingly serious. The intensification of industrial and agricultural activities has inevitably caused severe environmental pollution, with serious consequences for the atmosphere, waters, and soils (McGrath et al. 2017). Many governments have introduced legislation to set and limit emissions of

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pollutants in view of the rapid growth of public awareness of environmental problems (Sires et al. 2014). In the mid-1990s, the United Nations Environment Programme successfully reached consensus on the production, use, and emissions of persistent organic pollutants (POPs) (Rodan et al. 1999; Laine and Cheng 2007). Halogenated organic compounds, also known as organic halogens, are prevalent organic pollutants, and many of them have been classified as POPs. For example, various organochlorine insecticides, such as polychlorinated biphenyls (PCBs), polybrominated biphenyl ethers (PBDEs), and others, are used in the production of various commodities (Laine and Cheng 2007; Atashgahi et al. 2018). PCBs, which are widely and persistently present in the environment and accumulate through the food chain from aquatic organisms to fish and to humans, have adverse effects on various organisms and human beings (Beyer and Biziuk 2009; Zhang and Kelly 2018). A survey in 2006 reported that a number of species, e.g., soleus and sardines, contained PCBs and PBDEs (Fernandes et al. 2018). These compounds were also found in human milk and serum (Jiang et al. 2018a). Chlorophenols (CPs) are widely used in pesticides or to treat wood raw materials and have been identified as priority pollutants (Zhou et al. 2014). Most of them are recalcitrant, bactericidal, phytotoxic, and

carcinogenic; they have been detected in ground and surface waters, wastewaters, and soils (McGrath et al. 2017; Atashgahi et al. 2018). It is speculated that increasing amounts of waste waters containing CPs will be produced with continuing growth in their use. There are other pesticides that cause environmental pollution, such as Lindane, which is a common organochlorine pesticide and highly toxic and poses potential health risks to humans and animals, persists in aquatic environments, and is difficult to biodegrade (Dominguez et al. 2018a). Some halogenated organics have been found in the soil, contaminating the soil environment and posing great difficulties for soil remediation (Rodrigo et al. 2018). Another example is brominated compounds, which are present in natural water bodies. When a water body is disinfected by a chemical method, bromine participates in the reaction to produce more complex and toxic substances (Liu et al. 2018c; Zacs et al. 2018). Most of the halogenated flame retardants are brominated flame retardants, which include PBDEs. Long-term production of halogenated flame retardants in Shandong Province in China from 2007 to 2015 has led to large amounts of brominated compounds, including pentabromobenzene and pentabromotoluene, and PBDEs have been found in the sera of Shandong residents (Li et al. 2017; Ma et al. 2017b). Some congeners of PBDEs, such as 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153), and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), affect thyroid homeostasis, which causes endocrine disorders (Aznar-Alemany et al. 2017; Ma et al. 2017a; Miller et al. 2017; Glazer et al. 2018; Huang et al. 2018). Coddou et al. (2019) reported that 5-(3-bromophenyl)-1,3-dihydro-2Hbenzofuro[3,2-e]-1,4-diazepin-2-one (5-BDBD) has a certain influence on the central nervous system of mice. Polybromobenzene is hepatoxic and has been found in the liver of wild animals (Covaci et al. 2011). It can be seen that halogenated organics have a negative impact on the environment and endanger human health to a certain extent.

Many wastewater treatment techniques, e.g., incineration (Matsukami et al. 2014; Roszko et al. 2015), adsorption (Jiang et al. 2018b), biological methods (Kaczorek et al. 2016), and chemical methods (Tu et al. 2015; Cagnetta et al. 2016), have been developed for degrading halogenated organic pollutants to avoid further risks to the environment. However, many of these methods can produce toxic intermediates during the degradation process, e.g., incomplete advanced oxidation processes (Qi et al. 2018). For example, haloacetic acid and other harmful substances are produced in the treatment of wastewaters containing halogenated organics by ozone oxidation (Wang and Wang 2007). Electrochemical techniques are effective methods and have several advantages, namely mild reaction conditions, high efficiency, quick responses, and low cost; and the production of many of electrochemical techniques that are non-toxic or low-toxic compounds except some electrochemical oxidation techniques that produce halogenated compounds when breaking the C-X bond depends on effluent and the electrode material (Rodan et al. 1999; Wang and Wang 2007). Three main electrochemical procedures, classified according to their reaction pathways, are discussed in this review: electrochemical reduction and electrochemical oxidation. Some other combined techniques were discussed in this review. Figure 1 summarizes the electrochemical techniques used to degrade halogenated organics. Electrochemical reduction includes direct electrochemical reduction and indirect electrochemical reduction. And electrochemical oxidation includes direct electrochemical oxidation and indirect electrochemical oxidation. The cathodic indirect oxidation, one of advanced electrochemical oxidation processes, could be involved in indirect electrochemical oxidation. Combined techniques involve the combination of electrochemical reduction and electrochemical oxidation, namely electrochemical reduction-oxidation, electro-Fenton (EF), photoelectrochemical oxidation (PEC), and other combined techniques.

The electrode material has a variety of important roles in electrocatalysis. The electrode surface is the electrochemical reaction site and the location of the supply and reception of electrons in any electrolytic system. The properties of electrode materials, such as conductivity, significantly affect the number of electrons that participate in an electrochemical reaction. Their properties determine their suitability for different electrochemical approaches. High electrocatalytic activity, a long working lifetime, good physical and chemical stabilities and electrical conductivity, low cost and ease of fabrication, a large surface area with many active sites, and a wide operating potential window between the hydrogen and oxygen evolution reaction overpotentials are the prerequisites for electrode materials for use in electrochemical wastewater treatment. There are many important reviews of electrode materials or electrochemical techniques in different fields, such as decontamination of wastewaters containing synthetic organic dyes (Martinez-Huitle and Brillas 2009; Brillas and Martínez-Huitle 2014), electrochemical oxidation of organic pollutants (Martinez-Huitle and Ferro 2006), and the reduction of vat dyes (Roessler and Jin 2003), but no review of the degradation of halogenated organic pollutants by electrochemical methods that involve both electrochemical oxidation and electrochemical reduction has been published. This review focuses on the development of electrode methods for the degradation of halogenated organics. The mechanisms, degradation pathways, and electrode materials used in electrochemical techniques for degradation of halogenated organics are also discussed.

# Reductive dehalogenation via electrochemical reduction

In recent decades, electrochemical reduction has attracted increasing attention because of its excellent performance in the

**Fig. 1** Electrochemical technologies used for degradation of halogenated organics



reductive dehalogenation of halogenated organics. Electrochemical reductive dehalogenation reactions have been widely investigated for organic synthesis and environmental pollution abatement, especially for the abatement of polyhalogenated organic pesticides (Huang et al. 2017; Shundrin et al. 2017). This method provides two effective approaches to cleaving C-X (X = F, Cl, Br, I) bonds: direct electrochemical reduction and indirect electrochemical reduction. The nature of the electrode material determines which approach will perform better during the electrolytic process. Electrochemical oxidation can also be used to break the C-X bond, but it may produce toxic by-products via undesired reactions. In order to avoid undesired reactions, we added the cation exchange membrane in the process of electrochemical reduction to reduce the generation of toxic substances and completely remove all halogen atoms. Also, halogenated organics are toxic mainly because of the halogen atoms in their structures. Electrochemical reduction therefore has an advantage in destroying the toxicity of halogenated organics. Non-halogenated intermediates or final products are obtained by halogen atom removal.

A number of studies have explored appropriate cathode materials, the dehalogenation mechanism and pathway, and process optimization. An appropriate cathode material needs many characteristics, such as high electrocatalytic activity, long service lifetime, excellent selectivity, the ability to inhibit side effects, excellent electron transfer capacity, good electrochemical stability, good conductivity, low cost, and ease of preparation (Su et al. 2012; Zhang et al. 2018). The mechanisms and pathways of dehalogenation of different halogenated organics have also been investigated to identify the intermediates that may be produced during the electrochemical reduction process. The general dehalogenation mechanism is that electron transfer causes excessive negative charges at the C-X bond, causing it to break, forming halide ions and free radicals, and reacting with another electron and a proton to form an M (metal)-H bond. Taking hexachlorobenzene (HCB) as an example, the process of gradual dehalogenation was as Eq. (1) shown (Páramo et al. 2006). Process optimization is performed to obtain the highest dehalogenation efficiency. Table 1 gives data for different cathodes used in the electrochemical reduction of various halogenated organics under a range of conditions; the data were collected by surveying a large number of literature reports.

$$C_{6}Cl_{6}\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}HCl_{5}\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}H_{2}Cl_{4}\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}H_{3}Cl_{3}\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}H_{4}Cl_{2}\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}H_{5}Cl\frac{2e^{-},H^{+}}{-C\Gamma^{-}} \rightarrow C_{6}H_{6}$$

$$(1)$$

# **Direct electrochemical reduction**

Direct electrochemical reduction is a process that generates direct electron exchange between the cathode and an organic molecule on the cathode surface. Injection of one electron from the cathode into a halogenated organic molecule leads to fragmentation of a C-X  $\sigma$  bond (Bujes-Garrido et al. 2018). Dehalogenation can occur via two different mechanisms, i.e., stepwise bond breaking (Eqs. (2) and (3)) or concerted electron transfer (Eq. (4)) (Muthukrishnan et al. 2012; Brillas and Martínez-Huitle 2014).

 $\mathbf{RX} + \mathbf{e} = \mathbf{RX}^{-}$ 

$$\mathbf{R}\mathbf{X}^{\bullet} \rightarrow \mathbf{R}^{\bullet} + \mathbf{X}^{-} \tag{3}$$

$$\mathbf{R}\mathbf{X} + \mathbf{e}^{-} \rightarrow \mathbf{R}^{\bullet} + \mathbf{X}^{-} \tag{4}$$

Electron transfer competes with the hydrogen evolution reaction. Cathode materials should therefore have high catalytic activities to decrease the high overpotential, avoid hydrogen evolution, and contribute to dissociative electron transfer to C-X bonds (Huang et al. 2012). These cathode materials should therefore have not only the required basic characteristics but also a distinct high hydrogen-evolution overpotential when used in direct electrochemical reduction. Many cathode materials have been well studied, including metals, carbon materials, and hybrids based on active species.

Table 1 Electroch	nemical reduction of halogenate	d organics				
Cathode	Pollutant	Operating conditions	Current efficiency	Dehalogenation efficiency	Metabolites	Ref.
Direct electrochemic Ag	al reduction 1,2-Dichloroethane 1,1'2,2'-Tetrachloroethane TCA	10 mA cm <sup>-2</sup> , V = 65 mL, 4 mmol L <sup>-1</sup> initial organic concentration, 10 °C, Na <sub>2</sub> SO <sub>4</sub> electrolyte, pH 2.0 110 mA, V = 40 mL, 0.05 mol L <sup>-1</sup> initial organic concentration, 2 × 3 × 0.1 cm Ag electrode, 25 °C,	Near 95%	%06 <	No halogenated by-products <i>Cis-</i> and <i>trans-</i> 1,2-dichloroethylene Acetic acid	(Scialdone et al. 2010b) (Xu et al. 2012)
	Pentachlorophenol 2,4,6-Tribromophenol	0.5 mol $L^{-1}$ NaOH, 3 h 20 mA, 0.01 mol $L^{-1}$ initial organic concentration, $2 \times 3 \times 0.1$ cm Ag electrode, 298 K, in 0.5 mol $L^{-1}$ NaOH	11% (302 min) 67% (181 min)		21% pentachlorophenol, 79% tetraCl-phenol 1% monoBr-phenol, 99% phenol	(Xu et al. 2007)
	CIH2C-CH2CI	-2.9 V (potentiostatic) 4 mmol L <sup>-1</sup> initial organic 40 mA cm <sup>-2</sup> (amperostatic) concentration, 10 °C, 10 mA cm <sup>-2</sup> (ammeostatic) Na <sub>2</sub> SO./H <sub>2</sub> SO. 9H 2 0		15% (0.9 h) 51% (5.0 h) 65% (13.9 h)	No halogenated intermediates	(Scialdone et al. 2010a)
	Cl <sub>2</sub> HC-CHCl <sub>2</sub> Monochloroacetic acid	-1.6 V (potentiostatic) -1.6 V (potentiostatic) 15 mA cm <sup>-2</sup> (amperostatic) 400 km <sup>-2</sup> . V = 300 mL, 189 mg L <sup>-1</sup> initial organic concomption in Na - SC0 calcorneties 5 h	1.1%	95–96% (5.1 h) 96% (5.9 h) 27%	Trichloroethylene, vinyl chloride, 1,2-dichloroethane Acetic acid	(Scialdone et al.
Cu	Monochloroacetic acid Trichloroethylene	$400 \text{ Am}^{-2}$ , V = 300 ml, 189 mg L <sup>-1</sup> initial organic concentration, in Na <sub>2</sub> SO <sub>4</sub> electrolyte, 5 h 40 mA, 9.525 mm thick copper foam electrode,	< 0.5%	<10% 98%	Acetic acid	2014) (Scialdone et al. 2014) (Mao et al. 2012)
Graphite	Hexachlorobenzene	V = 270 mL with 260 mL of 0.042-mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> and 10 mL of 28–56 mg L <sup>-1</sup> trichloroethylene, 25–30 min V = 200 mL, 300 $\mu$ g L <sup>-1</sup> initial organic concentration, 42 cm <sup>2</sup> graphite cathode, pH 3.0, in 7 mmol L <sup>-1</sup>		30.8%	Pentachlorobenzene	(Wang and Lu 2014)
	Monochloroacetic acid	Na <sub>2</sub> SO <sub>4</sub> , 3 h 100 A m <sup>-2</sup> , V = 300 mL, 5 mmol L <sup>-1</sup> initial organic concentration, Na <sub>2</sub> SO <sub>4</sub> electrolyte, 5 h	4.4%	28%	Acetic acid	(Scialdone et al. 2014)
	Disinfection by-products	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$1.9 \pm 0.3$ to $4.1 \pm 0.2\%$	$\begin{array}{c} 69\pm1\%~({\rm Cl}~),\\ 86\pm9\%~({\rm L}),\\ 74\pm3\%~({\rm Br}~)\\ 72\pm1\%~({\rm Cl}~),\\ 79\pm6\%~({\rm Br}~)\\ 79\pm6\%~({\rm Br}~)\\ 76\pm4\%~({\rm Cl}~),\\ 92\pm4\%~({\rm Cl}~),\\ 92\pm4\%~({\rm Cl}~),\\ 92\pm4\%~({\rm Cl}~),\\ 62\pm4\%~({\rm Cl}~),\\ 62\pm6\%~({\rm $		(Radjenović et al. 2012)
Indirect electrochemi Pd-modified carbor	cal reduction 1 Haloacetic acids	0.3 mA cm <sup>-2</sup> , V = 100 mL, 100 cm <sup>2</sup> surface area of		00 ±4% (ΒΓ) <60 μg L <sup>-1</sup>		(Zhao et al. 2014)
paper Pd-Ti/TiO <sub>2</sub> nanotul	richloroethylene	cathode, 120 $\mu$ g L <sup>-1</sup> initial organic concentration 100 mA, V = 250 mL, 21 mg L <sup>-1</sup> initial organic concentration 0.01 mol 1 <sup>-1</sup> Na <sub>2</sub> SO, mH 7, 120 min		91%		(Xie et al. 2013)
Pd/PPy-CTAB/foar	n-Ni 2,4-Dichlorophenol	5 mA, V = 30 mL, 100 mg L <sup>-1</sup> mitial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , initial pH 2.2, $290 \pm 1$ K, 50 min	47.4%	100%	Phenol, cyclohexanone	(Sun et al. 2013)

Table 1 (continued)						
Cathode	Pollutant	Operating conditions	Current efficiency	Dehalogenation efficiency	Metabolites	Ref.
Pd/Ni Pd/Ag/Ni Pd/Ch/Ni	2-Chlorobiphenyl	1 mA cm <sup>-2</sup> , V = 75 mL, 1.78 mg cm <sup>-2</sup> Pd loading, 6.0 mg cm <sup>-2</sup> Ag or Cu loading, 0.053-mmol L <sup>-1</sup> initial organic concentration. 0.5 mol L <sup>-1</sup> NaOH 45 min		64.2% 92.5% 77 4%		(He et al. 2013)
Pd/CNTs/Ti	2,4,5-Trichlorobiphenyl	-1.0 V, 20 mg L <sup>-1</sup> initial organic concentration, 6-cm <sup>2</sup> surface area of cathode, in 0.05 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> , 6 h		90.0%	Dichlorobiphenyl, monochlorobiphenyl, binhenvl	(Chen et al. 2010)
Pd/Ti Pd/ <u>er</u> aphite				79.8% 52.7%		
Pd-Ni (SDBS)/Ti	2,4-Dichlorophenol	5 mA, V = 60 mL, 99.43 mg $L^{-1}$ initial organic concentration, 3.5 mmol $L^{-1}$ H <sub>2</sub> SO <sub>4</sub> and 0.05 mol $L^{-1}$ Na <sub>2</sub> SO <sub>4</sub> . 70 min	33.9%	100%	Phenol	(Sun et al. 2012a, b)
Pd/PPy/Ni	2,4-Dichlorophenol	5 mÅ, V = 30 mL, 99.43 mg $L^{-1}$ initial organic concentration. 70 min	33.6%	99.4%	Phenol	(Sun et al. 2010)
Pd/PPy-SLS/Ti	2,4-Dichlorophenol	5 mA, V = 30 mL, 99.43 mg $L^{-1}$ initial organic concentration, 0.05-mol $L^{-1}$ Na <sub>2</sub> SO <sub>4</sub> , initial pH 2.36, 70 min	33.9%	100%	Phenol	(Sun et al. 2012a)
Pd/PPY (PTS)/Ni	2,4-Dichlorophenol	5 mJ, V= 50 mL, 81.5 mg L <sup>-1</sup> initial organic concentration. 40 °C. 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> . 100 min		90.9%	Phenol, 2-chlorophenol, 4-chlorophenol	(Li et al. 2012)
Pd-Fe/graphene	4-Bromophenol	400 mA, 100 mg L <sup>-1</sup> initial 4-bromophenol concentration, 0.03 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , 60 min		100%	Phenol, benzoquinone, hydroquinone	(Xu et al. 2018b)
Pd <sub>58</sub> Ni <sub>42</sub> (SDBS)/PPy/Ti	Pentachlorophenol 2,4-Dichlorophenol	5 mA, 10 mg L <sup>-1</sup> initial pentachlorophenol concentration, 100 mg L <sup>-1</sup> initial 2,4-dichlorophenol concentration 0.05 mol L <sup>-1</sup> Na.SO, 90 min		100% (initial pH 2.0) 100% (initial pH 1.7)	Phenol	(Sun et al. 2014b)
Pd-Ni (CTAB)/Ti	Pentachlorophenol	3 mA, V = 30 mL, 10 mg $L^{-1}$ initial organic concentration, 298 ± 1 K, 0.05 mol $L^{-1}$ Na <sub>2</sub> SO <sub>4</sub> , initial pH 2 1 00 min		100%	Phenol	(Sun et al. 2014b)
Cu@Pd/Ti	Atrazine	1 mA cm <sup>-2</sup> , 5 mg L <sup>-1</sup> initial atrazine concentration, 0.1 mol L <sup>-1</sup> $H_2SO_4$ , 120 min		91.5%		(Chen et al. 2015)

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The first thing to note is that Ag has received widespread attention because of its excellent electrocatalytic activity in the direct cathodic reduction of halogenated organics (Rondinini et al. 2016; Bujes-Garrido et al. 2018). The electrocatalytic activity of a Ag cathode is higher than those of glassy carbon (GC), Cu, Pb, Pt, Ni, Fe, Pd, and Zn cathodes. Ag nanoparticles give similar or even better performances than bulk Ag (Lugaresi et al. 2014). Examination of the data in Table 1 shows that good results were obtained with this electrode material when dealing with 1,2-dichloroethane (Scialdone et al. 2010a, b), 1,1',2,2'-tetrachloroethane (Cl<sub>2</sub>HC-CHCl<sub>2</sub>) (Scialdone et al. 2010b), trichloroacetic acid (TCA) (Xu et al. 2012), 2,4,6-tribromophenol (Xu et al. 2007), pentabromophenol (Xu et al. 2007), and Cl<sub>2</sub>HC-CHCl<sub>2</sub> (Scialdone et al. 2010b), under corresponding experimental conditions. This can be attributed to the strong interactions between organic molecules and the Ag electrode, which make Ag an excellent electrocatalytic material for direct electric dehalogenation (Schröder et al. 2016). These interactions weaken the C-X bond and decrease the dechlorination activation energy, which is associated with a positive shift of the reduction potential (Jin and Ma 2013). However, the use of Ag with some halogenated organics, such as monochloroacetic acid (Scialdone et al. 2014), pentachlorophenol (Xu et al. 2007), and ClH<sub>2</sub>C-CH<sub>2</sub>Cl (Scialdone et al. 2010b), gives a low current efficiency or dehalogenation efficiency. The Ag electrode may be less effective in the degradation of these halogenated organics because of weak interactions between these organic molecules and the Ag electrode. Ag is usually deposited/fabricated as hybrids/alloys with other metals to improve the effectiveness of the dehalogenation reaction, e.g., Au/Ag (Schröder et al. 2016), porous Ag-Pd thin foam (PAPTF) (Jin and Ma 2013), and Pd/Ag/Ni (He et al. 2013). For example, Pd components in a porous PAPTF prepared by a rapid one-step electrodeposition method improve the electrocatalytic performance in the reductive dechlorination of TCA, but suppress it in high Pd contents (Jin and Ma 2013). The chemisorbed H atoms were formed on the cathode surface; it is attributed to the fact that H atoms is a powerful reducing agent to reductive debromination. Also, the H atoms reacted with halogenated organic matters of near the electrode surface to change the C-Cl bond to C-H (Vodyanitskii 2014), maybe because a low Pd content enables adsorption of hydrogen atoms, which play the leading role in attacking chlorine and Ag can weaken the C-Cl bond. The introduction of Ag or Cu can induce exposure of a relatively large surface area. He et al. (2013) obtained a more compact, uneven coating on the surfaces of Pd/Ag/Ni and Pd/Cu/Ni electrodes compared with that on a Pd/Ni electrode. As a result, the Pd/Ag/Ni electrode showed higher electrocatalytic activities and current efficiencies, which are attributed to the greater effective surface, a more appropriate Ag-H bond energy, and a strong ability to form bridged R-X-Ag intermediates (He et al. 2013).

Cu is considered to be a good alternative to Ag for cathode materials. Cu is widely distributed on the Earth and much cheaper than Ag (almost 10 times), although it has shown lower catalytic activities (Isse et al. 2012). A limited number of reports have been published on the direct electrochemical reduction of halogenated organics on Cu cathodes. Isse et al. (2012) explored the mechanism and electrocatalytic activity of Cu in the reduction of polychloromethanes (CCl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>) in dimethylformamide + 0.1 M Pr<sub>4</sub>NBF<sub>4</sub>. The principal reduction pathways occur via the sequence of reactions in Eqs. (5)–(7) (Isse et al. 2012).

$$CH_n Cl_{(4-n)} + e^{-} \rightarrow CH_n Cl_{(3-n)} + Cl^{-}$$
(5)

$$CH_nCl_{(3-n)} + e^{-} \rightarrow CH_nCl_{(3-n)}$$
(6)

$$C H_n Cl_{(3-n)} + HB \rightleftharpoons CH_{(n+1)} Cl_{(3-n)} + B^-$$
(7)

where HB is any proton donor present in the solution. The first step in this process is reductive cleavage of the C-Cl bond, with concerted dissociative electron transfer (Eq. (5)). The produced intermediate radical,  $\cdot$ CH<sub>n</sub>Cl<sub>(3-n)</sub>, is immediately reduced to  $^{-}$ CH<sub>n</sub>Cl<sub>(3-n)</sub> (Eq. (6)) and is then rapidly protonated by the proton donors present in the solution (Eq. (7)). The end product of the process is methane. The main function of Cu in this process is to reduce the C-Cl bond.

The Cu electrode and its hybrids show excellent electrocatalytic activities in the reductive cleavage of C-X bonds (Mao et al. 2012; Durante et al. 2014; Tan et al. 2018). As shown in Table 1, Mao et al. (2012) obtained a high chlorine elimination efficiency from trichloroethylene (almost 98%) by using a Cu foam electrode under the optimum conditions: Cu foam electrode of thickness 9.525 mm, current 40 mA, and 0.042mol  $L^{-1}$  Na<sub>2</sub>SO<sub>4</sub>. However, the Cu cathode gave poor degradation of monochloroacetic acid (Scialdone et al. 2014). Perhaps, the weak interactions between the organic molecules and Cu electrode lead to poor efficiency, similarly to the case for the Ag cathode. Cu is also used in hybrids/alloys with other metals, e.g., Pd-Cu nanoparticles (Durante et al. 2014), Cu/Fe (Chen et al. 2018), PVP-Cu/Fe (Li et al. 2018), s-Fe/Cu (Yu et al. 2017b), and Cu/Al (Huang et al. 2015). Note that Pd-Cu nanoparticles deposited on a GC substrate by a two-stage process show excellent electrocatalytic activity in the reductive cleavage of C-Cl bonds (Durante et al. 2014). The Pd-Cu nanoparticles essentially behave like bulk Pd, which is more active than Cu. The use of carbon or carbon-based materials for cathodes has also been investigated for electrocatalytic reductive dehalogenation; materials studied include borondoped diamond (BDD) (Zhao et al. 2012), graphite (Radjenović et al. 2012; Song et al. 2017; Flores et al. 2018), GC (Albo et al. 2017; Deng et al. 2017), and reticulated vitreous carbon (Ramirez-Pereda et al. 2018). An excess of surface negative charges can lead to breakage of C-X bonds via Eq. (4). Carbon-based materials are cheap and give high

overpotentials for hydrogen evolution, but their high resistance and low electrocatalytic activity make operating costs high (Su et al. 2012). Pure carbon electrodes have attracted little attention for reductive dehalogenation, because they give poor dehalogenation efficiencies (Brillas and Martínez-Huitle 2014; Wang and Lu 2014). For example, the data in Table 1 show that when graphite was used as the cathode, only 4.4%current efficiency and 28% abatement efficiency were observed in monochloroacetic acid degradation by Scialdone et al. (2014); 30.8% removal efficiency was observed for hexachlorobenzene (HCB) by Wang and Lu (2014). The electrocatalytic activity of a BDD electrode is higher than those of graphite and carbon paper electrodes in debromination (Zhao et al. 2012). However, for low concentrations of halogenated organics, carbon electrodes can give a sufficiently high dehalogenation efficiency. Radjenović et al. (2012) studied the degradation of 17 disinfection by-products (DBPs) at low microgram per liter concentrations with a resinimpregnated graphite cathode. The results show that polarization of resin-impregnated graphite cathode leads to the easier adsorption of hydrophilic DBPs on the electrode, and this increases the effectiveness of electrochemical reduction.

#### Indirect electrochemical reduction

This section reviews the electrocatalytic hydrodehalogenation (ECH) of halogenated organic compounds; ECH is the most popular method of indirect electrochemical reduction for reductive dehalogenation. ECH gives good selective removal of halogen atoms from halogenated compounds under mild conditions. The mechanism of ECH involves electrochemical reductive dehalogenation of adsorbed halogenated organic substrates by adsorbed hydrogen atoms (H<sub>ads</sub>) from hydrogen evolution or a hydrogen feed, via the reactions shown in Eq. (8)–(13) (Zhu et al. 2013; Shi et al. 2015).

 $2H_2O(H_3O^+) + 2e^- + M \rightarrow 2(H)_{ads}M + 2OH^-(H_2O)$  (8)

$$H_2 \rightarrow 2[H] \tag{9}$$

 $\mathbf{M} + [\mathbf{H}] \rightarrow (\mathbf{H})_{ads} \mathbf{M} \tag{10}$ 

$$R-X + M \rightarrow (R-X)_{ads}M \tag{11}$$

$$(R-X)_{ads}M + 2(H)_{ads}M \rightarrow (R-H)_{ads}M + HX$$
(12)

$$(R-H)_{ads}M \rightarrow R-H+M \tag{13}$$

where M is a metallic surface. In the first step,  $H_{ads}$  is formed on the cathode surface by electroreduction of water and/or from a hydrogen feed (Eqs. (8)–(10)). Then, a hydrodehalogenation reaction occurs between (H)<sub>ads</sub>M and the adsorbed halogenated organic, (R-X)<sub>ads</sub>M (Eqs. (11)–(13)). The (H)<sub>ads</sub> replaces the halogen atom in (R-X)<sub>ads</sub>M (Song et al. 2017). In other words, the reductive atomic hydrogen generated on the cathode surface is transferred for ECH during this reaction (Pan et al. 2008; Mao et al. 2014). ECH is considerably affected by the electrochemical characteristics of the cathode material and reaction conditions. The electrode plays a crucial role not only in supplying electrons for the reaction but also in forming H<sub>ads</sub>. Electrode materials with good catalytic activities that generate reductive atomic hydrogen are therefore required for ECH. Metal electrodes or modified electrode materials, e.g., Pb (Chen et al. 2010; Sun et al. 2013) and Ni (He et al. 2013), have excellent electrocatalytic activity for ECH of halogenated organics. Pd has a strong ability to adsorb/absorb hydrogen under ambient conditions and is considered to be one of the most effective hydrodehalogenation catalysts (Zhou et al. 2012; Zhao et al. 2013). However, the large-scale use of Pd in electrodes is limited by its high cost. To resolve this problem, noble-metal micro-/nanoparticles are loaded on a cathode substrate at high dispersity and on a large surface area to enable less expensive potential applications (Sun et al. 2013; Perini et al. 2014). The data in Table 1 show that, in general, Pd electrodes loaded with noble-metal micro-/nanoparticles or with other introduced metals show high catalytic activities in the ECH of halogenated organics; examples include Pd/ carbon paper (Zhao et al. 2014), Pd/Ni (He et al. 2013), Pd/ Ag/Ni (He et al. 2013), Pd/Cu/Ni (He et al. 2013), Pd-Fe/ graphene (Song et al. 2017; Xu et al. 2018b), Pd-Ti/TiO<sub>2</sub> nanotubes (TNTs) (Xie et al. 2013), Pd/polymeric pyrrolecetyl (PPy)-trimethyl ammonium bromide (CTAB)/foam-Ni (Sun et al. 2013), Pd/Ni foam (Yang et al. 2015), Pd-carbon nanotubes (CNTs)/Ni foam (Yang et al. 2015), Pd/CNTs/Ti (Chen et al. 2010), Pd/Ti (Chen et al. 2010), Pd/graphite (Chen et al. 2010), Pd-Ni (sodium dodecyl benzene sulfonate (SDBS))/Ti (Sun et al. 2012a), Pd/PPy/Ni (Sun et al. 2010), Pd/PPy-sodium dodecyl sulfonate (SLS)/Ti (Sun et al. 2012b), Polyanionic (PAC)-Pd/Fe (Huang et al. 2018), Re-Pdbimetallic (BC) (Xu et al. 2018a, b, c, d), palladiumpolypyrrole-foam nickel (Pd/PPy(PTS)/Ni) (Li et al. 2012), Pd/SBA-15 (Zhang et al. 2018), Pd<sub>58</sub>Ni<sub>42</sub>(SDBS)/PPy/Ti (Sun et al. 2014), Pd-Ni (cetyl trimethyl ammonium bromide (CTAB))/Ti (Sun et al. 2014b), Cu@Pd/Ti (Chen et al. 2015), and Rh-Pd (Xu et al. 2018d). Dehalogenation efficiencies of almost 100% have been achieved in ECH of many highly halogenated organics, such 2,4-DCP, pentachlorophenol, and TCA with Pd-based electrodes. Zero-valent iron has been incorporated with Pd to form Pd/Fe bimetallic catalysts, which show high catalytic activities in the degradation of halogenated organic compounds (Qiu et al. 2011; Shi et al. 2015; Song et al. 2017). Song et al. (2017) prepared graphene-supported Pd/Fe nanoparticle catalysts by a convenient method based on photocatalytic reduction under mild conditions. The average size of the  $Pd_{0.5}/Fe_{0.5}$  nanoparticles was  $6.75 \pm 0.05$  nm, with a uniform distribution on graphene. Figure 2 shows that the reduction peak of Pd<sub>0.5</sub>Fe<sub>0.5</sub>/graphene is stronger than those of  $Pd_{1,0}$ /graphene and  $Fe_{1,0}$ /graphene. Xu et al. (2018b) prepared



**Fig. 2** Cyclic voltammetry curves for Pd1.0/graphene, Fe1.0/graphene, and Pd0.5Fe0.5/graphene catalysts in 0.5-mol  $L^{-1}$  Na<sub>2</sub>SO<sub>4</sub> solution (pH = 12.8) with H<sub>2</sub> feed (Song et al. 2017)

a Pd-Fe cathode for degradation of 4-bromophenol (4-BP). The removal rate of 4-BP reached 100% at the cathode in 60 min. This enhancing effect may result from the Fe particles/nanoparticles performing different functions: (i) playing a significant role in the dispersion state of Pd particles; (ii) producing hydrogen, which can be collected by Pd to form  $H_{ads}$ ; (iii) performing direct reductive dehalogenation; and (iv) reducing the interfacial impedance (Zahran et al. 2013; Luo et al. 2014; Song et al. 2017).

Cathode substrates, such as GC (Qiu et al. 2011), graphene (Shi et al. 2014; Song et al. 2017), granular activated carbon (Zhao et al. 2014), Ti (Sun et al. 2014a, b; Su et al. 2017), Ti/TiO<sub>2</sub> (Xie et al. 2013), mesoporous N-doped carbon (Cui et al. 2017), Ni foam (Wu et al. 2017), and carbon fiber (Mao et al. 2014), have been considered as potential support materials for loaded metal nanoparticles for ECH. In recent years, many studies have focused on the modification of cathode substrates to improve the electrocatalytic performance. For example, the dispersion of metal catalysts on a support surface can be improved by introducing surface functionalities by chemical oxidation and acid/base and plasma treatment (Diaz et al. 2011; Sun et al. 2018). Doping carbonaceous materials with heteroatoms (e.g., N, B, or P) is an effective approach to improving the catalytic performance of a supported catalyst (Cui et al. 2017). For example, Perini et al. (2014) prepared an N-GC electrode modified by N<sup>2+</sup> and N<sup>+</sup> ion implantation, in which the nitrogen groups were placed near the new edges of the graphitic microstructure, as shown in Fig. 3. The nitrogen functional groups help to decrease the size and increase the dispersion of catalyst particles by affecting the nucleation and growth kinetics during Pd nanoparticle deposition. As a result, the catalytic activity of a Pd nitrogenimplanted electrode in C-Cl bond activation is higher than those of bulk Pd and Pd nanoparticles loaded on pristine GC electrodes (Perini et al. 2014).

# Oxidative degradation via electrochemical oxidation

Electrochemical oxidation is an advanced oxidation process with an excellent ability to degrade halogenated organics by powerful electrogenerated oxidants. Electrochemical oxidation is divided into direct oxidation and indirect oxidation, according to the production method and type of oxidant produced. Electrochemical reduction cannot degrade pollutants completely (Martinez-Huitle and Brillas 2009), but electrochemical oxidation can convert organic contaminants to  $CO_2$ and  $H_2O$  by electrochemical combustion or into simpler fragments by electrochemical conversion (Comninellis 1994).

In recent years, most studies of electrochemical oxidation of halogenated organics have focused on nanostructured electrode materials, the degradation mechanisms, corresponding kinetics, and the fate of the halogen. As in the case of electrochemical reduction, the electrodes used for electrochemical oxidation have several basic characteristics, such as high electrocatalytic activity, long service lifetime, good electrochemical stability, good conductivity, and ease of preparation. The pathways and mechanisms of the degradation of different halogenated organics during electrochemical oxidation have also been investigated to identify the intermediates or final products of the oxidation process to ensure that the products are environmentally safe (Sires et al. 2014). Table 2 shows data obtained at various electrodes for electrochemical oxidation of a range of halogenated organics; the data were collected by a literature survey.

#### **Direct electrochemical oxidation**

Direct electrochemical oxidation proceeds by a direct electron exchange between the anode and an organic molecule at the anode surface (Rao and Venkatarangaiah 2014). This process is described by two theoretical models developed by Comninellis (1994): electrochemical combustion and electrochemical conversion. Electrochemical combustion occurs directly at the anode with generation of physically adsorbed active oxygen (adsorbed hydroxyl radicals, •OH), and electrochemical conversion occurs directly at the anode with generation of chemisorbed active oxygen (oxygen in the oxide lattice,  $MO_{x+1}$  (Brillas and Martínez-Huitle 2014; Medeiros de Araújo et al. 2014). Physically adsorbed •OH on the anode surface is formed by oxidation of water molecules (Eq. (14)). The adsorbed •OH can interact with an active anode to form a chemisorbed higher oxide  $MO_{x+1}$  (Eq. (15)). If no oxidizable organics are present, the active oxygens decompose and oxygen is evolved (Eqs. (16) and (17)). When target organic substrates are present, the adsorbed  $\cdot$ OH and MO<sub>x+1</sub> oxidize the organic compounds that are adsorbed on the anode surface (Eqs. (18) and (19)). In general, physically adsorbed •OH is more beneficial for oxidizing organics than is oxygen in the **Fig. 3** Ball-and-stick model of the different chemical species obtained after ion implantation in GC (Perini et al. 2014)



Pyridinic defects

oxide lattice. The complete degradation and selective conversion of the organic substrate are shown schematically in Fig. 4.

$$MO_X + H_2O \rightarrow MO_X(^{\bullet}OH) + H^+ + e^-$$
(14)

$$MO_{X}(^{\bullet}OH) \rightarrow MO_{X+1} + H^{+} + e^{-}$$
(15)

$$MO_X(^{\circ}OH) \rightarrow 1/2O_2 + MO_X + H^+ + e^-$$
 (16)

$$MO_{X+1} \rightarrow 1/2O_2 + MO_X \tag{17}$$

$$R + MO_X(OH)_Z \rightarrow z/2CO_2 + zH^+ + ze^- + MO_X$$
(18)

$$\mathbf{R} + \mathbf{MO}_{\mathbf{X}+1} \rightarrow \mathbf{RO} + \mathbf{MO}_{\mathbf{X}} \tag{19}$$

Electrochemical oxidation involves side reactions. For example, oxygen evolution occurs when the reaction potential reaches the oxygen evolution overpotential, and this increases energy consumption. Direct oxidation should perform at a potential well below the oxygen evolution overpotential (Rao and Venkatarangaiah 2014). An anode with a high overpotential for oxygen evolution is required to ensure a high degradation efficiency, to avoid wasting energy on water splitting (Chen 2004). The choice of anode material is therefore crucial. Various anode materials have been investigated to improve the performance of direct oxidation for degradation of halogenated organics. The materials tested include single metals, such as Pt (Liu et al. 2018b) and Au (Candu et al. 2017), metallic oxide, such as  $PbO_2$  (Gong et al. 2018), ZrO<sub>2</sub> (Yao et al. 2012; Poungchan et al. 2016), and IrO<sub>2</sub> (Guzman-Duque et al. 2014; Markou et al. 2017), carbon material, such as CNTs (Khene and Nyokong 2012), BDD (Lan et al. 2017; Flores et al. 2018), and GC (Gonzalez et al. 2013), and some materials of hybrids based on active species, such as dimension stable anodes (DSAs) (Brillas and Martínez-Huitle 2014; Markou et al. 2017), Si/BDD (Madsen et al. 2014), and Ti/Pt<sub>10</sub>-Ir<sub>10</sub> (Madsen et al. 2014). The most widely investigated materials are Pt, PbO<sub>2</sub>, CNT, BDD, and their hybrids. These were discussed here in more detail.

Pt metal electrodes have been extensively studied. They show good electrocatalytic activity in direct oxidation of many halogenated organics, e.g., 3-bromobenzoic acid (3-BBA) (Ye et al. 2013), imidacloprid (Turabik et al. 2014), iopamidol (Liu et al. 2018b), halogenated nitrobenzene (Ma et al. 2017a), clofibric acid (Sires et al. 2006), and 4-CP (Ma et al. 2009). Sirés et al. (2006) reported that clofibric acid was destroyed more rapidly on a Pt electrode than on a BDD electrode. This is attributed to stronger adsorption of clofibric acid on the Pt surface than on the BDD surface, which enhances the oxidation reaction with •OH. However, the use of Pt electrodes is restricted because of their low oxygen evolution potential, which results in passivation by pollutants or intermediates (Zhao et al. 2009). The data in Table 2 show that many intermediates and products remain stable in solution when Pt is used, resulting in only 30% total organic carbon (TOC) removal efficiency (Sires et al. 2006). Garza-Campos et al. (2014) reported that a TOC removal efficiency of 46% was obtained in degradation of the herbicide atrazine with a Pt electrode. Another study showed that an insoluble oligomer remained on the Pt electrode surface, which could poison the Pt electrode and result in gradual loss of its electrochemical activity (Ma et al. 2009).

One alternative is the PbO<sub>2</sub> electrode. PbO<sub>2</sub> is a good anode material because of its excellent electrical conductivity, high overpotential for oxygen evolution, and low cost (Jiang et al. 2011). Cao et al. (2009) and Duan et al. (2012) investigated the use of a PbO<sub>2</sub> electrode for 4-CP elimination. They

Table 2 Electr	ochemical oxidation of halogenat	ed organics				
Anode	Pollutant	Operating conditions	Organics removal efficiency	TOC removal efficiency	Metabolites	Ref.
Direct electroch, Pt	emical oxidation Clofibric acid	100 mA cm <sup>-2</sup> , V = 100 mL, 179 mg L <sup>-1</sup> initial clofibric acid, 35 °C, 3 cm <sup>2</sup> surface area of anode, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , 7 h		30%	<ul> <li>4-Chlorophenol, 4-chlorocatechol,</li> <li>4-chlororesorcinol,</li> <li>hydroquinone, p-benzoquinone</li> <li>1,2,4-benzenetriol tartronic,</li> <li>maleic, fumaric, formic,</li> <li>2-hydroxyisobutyric, pyruvic,</li> <li>oxalic acids</li> </ul>	(Ma et al. 2009)
$PbO_2$	4-Chlorophenol	25 mA cm <sup>-2</sup> , 8 mmol L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 6.3. 2 h	87.3%			(Duan et al. 2012)
	4-Chlorophenol	30 mJ cm <sup>-2</sup> , V = 200 mL, 50 mg L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO, 30 °C $2$ h	78.5%			(Wang et al. 2018a)
CNT-PbO <sub>2</sub> CTAB-CNT-PI	4-Chlorophenol 502	30 mA cm <sup>-2</sup> , V = 200 mL, 50 mg L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , 30 °C, 2 h	82.9% 92.8% 100%			(Wang et al. 2018a)
Er-chitosan-F modified Pb(	2, 2,4-Dichlorophenol 0 <sub>2</sub>	5 mA cm <sup>-2</sup> , V = 180 mL, 90 mg L <sup>-1</sup> initial organic concentration, 15 cm <sup>2</sup> surface area of anode $nH 3.0, 20 \circ C$	95% after 120 min	53% after 360 min		(Xu et al. 2017)
F-doped PbO <sub>2</sub>	4-Chlorophenol	25 mA cm <sup>-2</sup> , 1.03 g L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH	96.2%			(Duan et al. 2012)
BDD	Hexachlorocyclohexane	$^{0.5, 2}_{0.0, 2}$ M $^{0.2, 2}_{0}$	%06			(Scialdone et al. 2012)
	3-Chlorophenol	$20 \text{ A cm}^{-2}$ , 100 mg L <sup>-1</sup> initial 3-chlorophenol concentration, 0.1 MPa, 0.1 mol T <sup>-1</sup> Na. SO. 6 h		87%		(Wang et al. 2012b)
	Methylene blue	20 mA cm <sup>-2</sup> flow rate: 180 dm <sup>3</sup> h <sup>-1</sup> , 0.5 mol 1 $^{-1}$ Na.SO. 40 $^{\circ}$ 7.50 min		100% about 130 min		(Panizza et al. 2007)
	Dodecylpyridinium chloride	5 mA cm <sup><math>-2</math></sup> , 75 mg L <sup><math>-1</math></sup> initial organic concentration, flowrate of 300 dm <sup>3</sup> h <sup><math>-1</math></sup> , 05 m <sup><math>-1</math></sup> , 05 m <sup><math>-1</math></sup>	100%	> 96%		(Panizza et al. 2016)
	2-Chlorophenol	900 A m <sup>-2</sup> , V = 1 L, 2 g L <sup>-1</sup> initial organic concentration, 0.007 m <sup>2</sup> surface area of anode, 4 h		100% in Na <sub>2</sub> SO <sub>4</sub> 4 mmol L <sup>-1</sup> of TOC remained in NaCl electrolyte		(Song et al. 2018)
Cathodic indirec	t oxidation Clofibric acid			39%		(Kim et al. 2016)

Table 2 (continued)						
Anode	Pollutant	Operating conditions	Organics removal efficiency	TOC removal efficiency Metabolite	SS	Ref.
Carbon-PTFE (cathode)		100 mA cm <sup>-2</sup> , V = 100 mL, 3 cm <sup>2</sup> surface area of a gas-diffusion cathode, 179 mg L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 3, 6 h, 35 °C, feeding O,				
Pd/activated carbon (cathode)	4-Chlorophenol, 2,4-dichlorophenol pentachlorophenol	39 mA cm <sup>-2</sup> . V = 100 mL, 16 cm <sup>2</sup> surface area of a gas-diffusion cathode, 100 mg L <sup>-1</sup> initial organic concentration, in 0.1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 7, 100 min	100%			(Wang et al. 2010
	2,4-Dichlorophenol	39 mA cm <sup>-2</sup> , $V = 50$ mL, 16 cm <sup>2</sup> surface area of a gas-diffusion cathode, 100 mg L <sup>-1</sup> initial organic concentration, in 0.1 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 7, 160 min		>76% Hydroquir maleic, malonic formic a	none, benzoquinone, fumaric, crylic, 2, oxalic, acetic, acids	(Bach et al. 2010)
BDD	Dye Procion Red MX-5B	10 mA cm <sup>-2</sup> , $100$ mg L <sup>-1</sup> initial organic concentration, 3 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , 25 °C		100%		(Cotillas et al. 2018a)



**Fig. 4** Reactions involved in oxidation of organics on electrode surface (O = active oxygen in oxide lattice; R = organics) (Comninellis 1994)

reported that direct electrochemical processes with a pure PbO<sub>2</sub> electrode decreased the 4-CP contents by 87.3 and 78.5%, respectively, in 2 h. The oxygen release ability of PbO<sub>2</sub> is the same as that of SnO<sub>2</sub>, but the working lifetime and pollutant removal efficiency of PbO2 are higher than those of SnO<sub>2</sub> (Duan et al. 2016; Wang et al. 2018a). However, the use of PbO<sub>2</sub> electrodes is limited by several disadvantages, such as a relatively low electrocatalytic activity, short service lifetime, and potential release of toxic Pb<sup>2+</sup> ions in strongly acidic solutions at high current densities (Brillas and Martínez-Huitle 2014; Duan et al. 2016; Qiao et al. 2018). For these reasons, many recent studies have focused on the use of PbO<sub>2</sub> anodes that have been modified with doping ions, other metal particles, or surfactants (Liu et al. 2014). Various studies have shown that better performances in the degradation of halogenated organics can be achieved with modified PbO<sub>2</sub> electrodes, e.g., CNT-PbO<sub>2</sub> (Duan et al. 2012), CTAB-CNT-PbO<sub>2</sub> (Duan et al. 2012), LAS-CNT-PbO<sub>2</sub> (Duan et al. 2012), Ce-PbO<sub>2</sub> (Qiao et al. 2018), Er-chitosan-F-modified PbO<sub>2</sub> (Wang et al. 2010), F-doped PbO<sub>2</sub> (Cao et al. 2009), multiwalled (MW)CNTs-OH-PbO<sub>2</sub> (Xu et al. 2017), and GNS-PbO<sub>2</sub> (Duan et al. 2017) electrodes. Wang et al. (2010) compared the performances of three different modified PbO<sub>2</sub> electrodes, namely an Er-modified PbO<sub>2</sub> electrode, a Fmodified PbO<sub>2</sub> electrode, and an Er-chitosan-F-modified PbO<sub>2</sub> electrode, in the treatment of 2,4-DCP in aqueous solution. The Er-chitosan-F modified PbO<sub>2</sub> electrode gave the best result: the removal rates of 2,4-DCP and TOC were 95% in 120 min and 53% in 360 min, under the conditions current density 5 mA cm<sup>-2</sup>, solution volume 180 mL, and initial 2,4-DCP concentration 90 mg  $L^{-1}$ . The service lifetimes of modified PbO<sub>2</sub> electrodes, such as MWCNTs-OH-PbO<sub>2</sub> (Xu et al. 2017), F-PbO<sub>2</sub> (Cao et al. 2009), CNTs-Bi-PbO<sub>2</sub> (Chang et al. 2014b), PbO<sub>2</sub>-ZrO<sub>2</sub> (Yao et al. 2012), and GNS-PbO<sub>2</sub> (Duan

**Fig. 5** Electrode stability tests. **a** Electrode potential (vs Ag/AgCl) vs time for electrolysis (1 A cm<sup>-2</sup>, 60 °C) of 2-mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> with PbO<sub>2</sub>, Bi-PbO<sub>2</sub>, CNTs-PbO<sub>2</sub>, and CNT-Bi-PbO<sub>2</sub> electrodes as anode (Chang et al. 2014). **b** Changes in anode potential with electrolysis time in accelerated lifetime tests (Duan et al. 2017)



et al. 2017), are several times greater than that of unmodified electrode. The results of stability tests on the CNT-Bi-PbO<sub>2</sub> electrode are showed in Fig. 5a. The working lifetime of the CNT-Bi-PbO<sub>2</sub> electrode is 4.16 times longer than that of the PbO<sub>2</sub> electrode (Chang et al. 2014b). The working lifetime of the GNS-PbO<sub>2</sub> electrode is 1.93 times longer than that of a traditional PbO<sub>2</sub> electrode (Fig. 5b) (Duan et al. 2017). When the concentration of ZrO<sub>2</sub> nanoparticles reached 60 mg L<sup>-1</sup>, the PbO<sub>2</sub>-ZrO<sub>2</sub> electrode achieved a working lifetime of 141 h, which is almost four times that of the pure PbO<sub>2</sub> electrode (Yao et al. 2012). The presence of CNT and Bi in the CNTs-Bi-PbO<sub>2</sub> improved the morphological structure and increased the oxygen evolution overpotential; this decreased oxygen evolution, which is one of the major reasons for stripping and dissolution of the PbO<sub>2</sub> film (Chang et al. 2014b).

Carbon materials, e.g., CNTs (Xu et al. 2017), GC (Fernandez et al. 2014), and BDD (Dominguez et al. 2018b), have been widely investigated in electrochemical oxidation because of their high surface area, electrical conductivity, chemical stability, and low cost (Zhai et al. 2011). Activated carbon, CNTs, and GC are usually used as catalyst supports and are involved in formation of new active sites (Chang et al. 2014a). There are few reports of electrochemical oxidation of halogenated organics on GC electrodes (Duan et al. 2013; Fernandez et al. 2014). However, CNTs are considered to be a special and ideal template as a carrier for nanoparticles and give good dispersion (Wildgoose et al. 2006). For example, Pogacean et al. (2014) suggested that doubleand multi-walled CNTs have larger active surface areas than single-walled CNTs and give greater interfacial transfer of electrons. There is also increasing interest in combining CNTs with other electrode materials to improve the electrochemical properties (Duan et al. 2012; Chang et al. 2014a). Duan et al. (2012) have focused on doping CNTs into PbO<sub>2</sub> films by electrodeposition to fabricate an anionic surfactantlauryl benzene sulfonic acid sodium (LAS)-CNTs-PbO2 electrode. As shown in Fig. 6, the LAS-CNTs-PbO<sub>2</sub> electrode performed better than other PbO2-based electrodes in 4-CP degradation and TOC removal.

Another important carbon material, BDD, is a special anode material. It has no catalytically active sites for reactant adsorption, but it shows excellent electrochemical stability and a wide potential window in aqueous solution (Brillas and Martínez-Huitle 2014; Ltaief et al. 2018). Only physically adsorbed active oxygen species are formed on the surface of the BDD electrode, by water electrolysis, and then electrochemical combustion occurs between the physically adsorbed •OH and halogenated organics (Martinez-Huitle and Brillas 2009); •OH radicals are therefore the main species involved in pollutant degradation (Guzman-Duque et al. 2014). Anodic oxidation with a BDD electrode has been used to degrade many types of halogenated organics, including 3-CP (Ltaief et al. 2018), 5-fluorouracil (Ochoa-Chavez et al. 2018), 4-CP (Wang and Li 2012), 2,4-DCP (Wang and Li 2012), 2,4dichlorophenoxyacetic acid (2,4-D) (Souza et al. 2016), 5fluorouracil (Siedlecka et al. 2018), 2,4,6-trichlorophenol (2,4,6-TCP) (Wang and Li 2012), HCH (Dominguez et al. 2018a), triclosan (TCS) (Sola-Gutierrez et al. 2018), methylene blue (MB) (Panizza et al. 2007), dodecylpyridinium chloride (Panizza et al. 2016), crystal violet (Klidi et al. 2019), and Cl<sub>2</sub>HC-CHCl<sub>2</sub> (Scialdone et al. 2012). Many studies have shown that direct electrochemical oxidation with a BDD anode can remove the most of the halogenated organic compounds. For example, Ltaief et al. (2018) reported 3-CP removal of about 87% in 6 h using BDD as the anode at 0.05 A and 0.1 MPa, with an initial 3-CP concentration of  $100 \text{ mg L}^{-1}$ . Turabik et al. (2014) reported that anodic oxidation of imidacloprid with a BDD anode achieved a high mineralization efficiency (91%) and complete TOC removal in 2 h. Nearly complete mineralization was obtained by anodic oxidation with a BDD anode (Scialdone et al. 2014; Turabik et al. 2014). Vallejo et al. (2013) reported complete mineralization in 4 h of 2-CP in two different electrolytes (NaCl and  $Na_2SO_4$ ) by using a BDD anode of surface area 70 cm<sup>2</sup>, a current density of 900 A cm<sup>-2</sup>, and a 2-CP concentration of  $2 \text{ g L}^{-1}$ . To further improve the performance, BDD was deposited on various supports, such as Nb, Ti, W, and Si to form Nb/BDD, Ti/BDD, Si/BDD, and p-Si/BDD electrodes (Brillas and Martínez-Huitle 2014; Salatiel et al. 2019). These electrodes have been widely used to degrade halogenated organics and have shown excellent electrochemical stability. Muff et al. (2012) studied electrochemical oxidation of complex polluted



groundwater containing chlorinated solvents with two different anodes, namely  $Ti/Pt_{90}$ -Ir<sub>10</sub> and Si/BDD. The Si/BDD electrode gave better TOC removal and full mineralization of the organic groundwater contaminants. A similar result is shown in Fig. 7 (Madsen et al. 2014). However, the unacceptably high costs of these metal substrates (Nb, Ti, W, and Si) restrict their applications (Martinez-Huitle and Ferro 2006).

#### Indirect electrochemical oxidation

Indirect electrochemical oxidation is a well-known and effective technique for oxidizing inorganic and organic pollutants with electrochemically generated oxidants, such as active chlorine, sulfate free-radicals ( $SO_4^{-}\bullet$ ),  $\bullet OH$ , H<sub>2</sub>O<sub>2</sub>, and ozone. However, anodic oxidation in chlorine-free wastewater



Fig. 7 TOC removal in two cells; inset: first-order kinetic plot (Madsen et al. 2014)

produces active chlorine species, such as free chlorine and chlorine-oxygen species. Organic pollutants can be oxidized to small intermediate products or completely mineralized (Martinez-Huitle and Brillas 2009; Song et al. 2018). However, the indirect electrochemical oxidation method of electrogenerated active chlorine is unsuitable for the degradation of most wastewater containing halogenated organics because of possible production of residual chlorine. In contrast, indirect electro-oxidation with electrogenerated hydroxyl radicals or  $H_2O_2$  is feasible. In this review, the cathodic indirect oxidation was mainly discussed.

In electrochemical oxidation, halogenated organics are degraded with oxidants, such as  $H_2O_2$ , •OH,  $SO_4^-$ •, and Cl•. Note that in cathodic indirect oxidation with  $H_2O_2$  and •OH, these species are generated in the cathode chamber.  $H_2O_2$  is a green chemical reagent and is widely used for wastewater treatment. It can be formed via two-electron reduction of oxygen on the cathode surface (Moreira et al. 2017). Eq. (20) describes the reduction of dissolved oxygen from injected compressed air or oxygen gas, or water oxidation to generate  $H_2O_2$  (Sires et al. 2014). Furthermore,  $H_2O_2$  can be converted to •OH, as shown in Eq. (21) (Cheng et al. 2003). Generation of  $H_2O_2$  via this reaction has been confirmed by electron spin resonance spectroscopy (Bian et al. 2014a).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{20}$$

$$H_2O_2 + e^- \rightarrow OH^- + HO^{\bullet}$$
(21)

Much research has focused on the use of a special type of cathode, namely gas-diffusion cathodes, for this reaction (Sires et al. 2014). The nature of the electrode material is an import factor in the electrochemical reduction of oxygen because it affects the reduction potentials and currents and oxygen adsorption (Sawyer et al. 1982). Carbon materials are suitable for commercial applications because most of them are cheap and have high surface areas. In recent years, research in this field has centered on carbon or carbon-based materials for degradation of halogenated organics, e.g.,

graphene (Song et al. 2017; Xu et al. 2018b), carbon-poly (tetrafluoroethylene) (PTFE) (Moreira et al. 2014), carbon felt/fiber (Zhang et al. 2018), CNTs (Kim et al. 2016), BDD (Cotillas et al. 2017, 2018a), and activated carbon (Wang et al. 2012b). For example, a Pd-Fe/graphene catalytic cathode gives a high removal rate for 4-BP by producing •OH in the cathode chamber, and 100% mineralization is achieved in 1 h (Xu et al. 2018b). Cotillas et al. (2017) studied the effects of sodium chloride and sulfate on the degradation of clopyralid with BDD electrode; the result showed that the addition of sodium chloride and sulfate had no significant effect on the degradation rate of chloride. Carbon-based materials with supported noble metal show excellent electrocatalytic activity and electrogeneration of H<sub>2</sub>O<sub>2</sub>; this is attributed to the provision of highly active sites for oxygen reduction. Noble metals, such as Pd and Au, are good choices for constructing gas-diffusion cathodes, but because of their high cost they are used as electrode modifiers (Sljukic et al. 2005). Pd can accelerate the two-electron reduction of oxygen to H<sub>2</sub>O<sub>2</sub> (Wang and Wang 2009). Wang and Wang (2007) prepared a Pd-modified activated carbon (Pd/C) catalyst with a Pd loading of 1.3 at% and Pd particles of average size 4.0 nm. As shown in Fig. 8, when the Pd/C gas-diffusion cathode system was used, the 4-CP and COD removal efficiencies were higher than those obtained with a carbon-PTFE cathode system. The catalytic ability of the Pd/C gas-diffusion electrode system is clearly better than that of the C/PTFE gas-diffusion electrode system. Many types of chlorophenol, e.g., 4-CP, 2,4-DCP and pentachlorophenol, have been degraded with the Pd/C gas-diffusion electrode system via a combination of cathodic indirect oxidation and electrochemical oxidation; almost 100% organic removal efficiencies were achieved and highly TOC removal efficiencies were obtained under various conditions by this combined process (Wang and Wang 2008; Wang et al. 2012a; Bian et al.



**Fig. 8** Removal of 4-CP in the cathodic compartment ( $\blacksquare$ ,  $\blacktriangledown$ ) and anodic compartment ( $\bullet$ ,  $\blacktriangle$ ) and COD in cathodic compartment ( $\square$ ,  $\neg$ ) and anodic compartment ( $\circ$ ,  $\triangle$ ), during electrolysis with an air feed by C/PTFE gas-diffusion electrode system ( $\blacksquare$ ,  $\bullet$ ,  $\square$ ,  $\circ$ ) and Pd/C gas-diffusion electrode system ( $\blacktriangledown$ ,  $\bigstar$ ,  $\neg$ ,  $\triangle$ ) (Wang and Wang 2007)

2014a). The combined process will be discussed in the electrochemical reduction-oxidation section.

## **Combined techniques**

Some combined and hybrid electrochemical processes have been proposed to improve the removal efficiency of halogenated organic contaminants and reduce the application cost. They include the combination of electrochemical reduction-oxidation, EF, and irradiated electrochemical oxidation, as well as the use of biochemical method, which are summarized in Table 3 and discussed as following.

#### **Electrochemical reduction-oxidation**

In general, the oxidants produced on the anode surface can mineralize most organic matter (Wang and Wang 2007; Flores et al. 2018). However, total mineralization of halogenated organics usually cannot be achieved (Song et al. 2017; Xu et al. 2018b). Toxic intermediates can be produced under incomplete mineralization, as mentioned above. For example, the aromatic nucleus of a chlorinated organic pollutant is usually opened, forming many chlorinated aliphatic intermediates (Hirvonen et al. 2000; Jia et al. 2018). In the disposal of highly concentrated and poisonous organic wastes, total mineralization is not necessary, but toxic intermediate formation before biological processes is undesirable. Electrochemical pretreatment can be used to improve the effluent biodegradability and/ or decrease the toxicity (Fontmorin et al. 2014). A process that combines electrochemical reduction and electrochemical oxidation has been developed to resolve this problem and improve the removal efficiency when dealing with halogenated organics (Wang and Wang 2007; Scialdone et al. 2012; Moussavi and Rezaei 2017). In this process, the removal of halogenated organics was usually accomplished by the interaction of cathodic compartment and anodic compartment. Non-halogenated intermediates are formed in the cathodic compartment after the halogen atoms have been selectively released from the halogenated organics by electrochemical reduction. This significantly decreases the toxicity. Simultaneously or subsequently, the intermediates are oxidized indirectly or directly in the anodic compartment and/or the cathodic compartment by electrochemical oxidation. Finally, the halogenated organics are converted into intermediates that are biodegradable or easily biodegradable, even to  $H_2O$  and  $CO_2$ . There are two main routes for performing the combined process: (i) direct electrochemical reduction coupled with electrochemical oxidation and (ii) indirect electrochemical reduction coupled with electrochemical oxidation. The mechanisms of (i) and (ii) were described by taking chlorine as an example; dechlorination is carried out in the cathode chamber by direct and indirect reduction; due to the

Table 3 Combined techni	ques of halogenated organics					
Anode	Pollutant	Operating conditions	Organics removal efficiency	TOC removal efficiency	Metabolites	Ref.
Electrochemical reduction-c Anode-cathode	xidation					
BDD-Ag	1,2-Dichloroethane	20 mA cm <sup>-2</sup> , V = 65 mL, 0.4 mg L <sup>-1</sup> initial pollutant concentration, in 0.035 mol L <sup>-1</sup> Na.S.O. $\text{mH} \ge 10^{\circ}\text{C}$	close 100%			(Scialdone et al. 2010a)
	1,1',2,2'-Tetrachloroethane	20 mA cm <sup>-2</sup> , V = 65 mL, 0.67 mg L <sup>-1</sup> initial pollutant concentration, in 0.035 mol L <sup>-1</sup> Na.SO. $\mu$ H 2 10 °C	96%			(Scialdone et al. 2012)
	1,1',2,2'-Tetrachloroethane	15 mA cm <sup>-2</sup> , 0.15 mg L <sup>-1</sup> initial pollutant concentration, in 0.035 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , $M_{12}$	> 99.9%			(Scialdone et al. 2012)
Ti/IrO <sub>2</sub> /RuO <sub>2</sub> -Pd-Fe/gra	phene 4-Bromophenol	25 mA cm <sup>-2</sup> , V = 150 mL, 100 mg L <sup>-1</sup> initial concentration, in 0.03 mol L <sup>-1</sup> No. SO, $= 11.7$ , so min	100% in catholytes 99.5% in		Aromatic intermediates (phenol), organic acids	(Xu et al. 2018b)
Ti/IrO <sub>2</sub> /RuO <sub>2</sub> -Pd/C gas-diffusion	4-CP 2,4-DCP PCP	39 mA cm <sup>-2</sup> , V = 100 mL, 100 mg $L^{-1}$ initial concentration, in 0.1 mol $L^{-1}$ Na <sub>2</sub> SO <sub>4</sub> , pH 7, 200 min	anotyce 100% (60 min) 100% (80 min) 100% (200 min)	> 80% > 90% > 80%		(Wang et al. 2012a)
Electro-Fenton			~			
BDD	Imidacloprid	400 mA, V = 200 mL, 25.57 mg L <sup><math>-1</math></sup> initial organic concentration, 24 cm <sup><math>2</math></sup> surface area of anode, 0.05 mol L <sup><math>-1</math></sup> Na <sub>2</sub> SO <sub>4</sub> , 2 h	94%		Formic, acetic, oxalic, glyoxylic acids inorganic anions CI <sup>-</sup> , NOA <sup>5-</sup> NH <sup>44</sup>	(Ma et al. 2017a)
	Cyanazine	100 mA cm <sup>-2</sup> , V = 100 mL, 110 mg L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 3, 480 min, 35 °C, 0.5 mmol L <sup>-1</sup> Fe <sup>2+</sup> , feeding O <sub>2</sub> at 12 mL min <sup>-1</sup>		95%		(Garcia et al. 2014)
	2,4-Dichlorophenoxyacetic acid	31 mA cm <sup>-2</sup> , V = 3 L, 20–22 °C, 60 mg L <sup>-1</sup> initial organic concentration, feeding O <sub>2</sub> with 1 L min <sup>-1</sup> , 64 cm <sup>2</sup> surface area of electrode, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 3.0, 0.7 mmol L <sup>-1</sup> Fe <sup>2+</sup> , 120 min		81-83%	<ol> <li>2, 4-Dichlorophenol,</li> <li>4, 6-dichlororesorcinol,</li> <li>chlorohydroquinone,</li> <li>chloro-p-benzoquinone,</li> <li>hydroquinone,</li> <li>hydroxylated,</li> <li>derivatives</li> </ol>	(Sires et al. 2007)
	1,2-Dichloroethane	300 mA, V = 130 mL, 0.4 mg L <sup>-1</sup> initial organic concentration, 0.035 mol L <sup>-1</sup> NaSO. $\rightarrow$ H 3 0.10 °C 480 min	100% (420 min)		Acetic, formic, oxalic	(Randazzo et al. 2011)
	1,1,2,2-Tetrachloroethane	300 mA, 0.67 mg L <sup>-1</sup> initial organic concentration, 0.035 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 3.0, 10 °C, 480 min	100% (420 min)			(Randazzo et al. 2011)
Pt	Clofibric acid			%2000 0%20 0%20 0%20 0%20 0%20 0%20 0%2		

Anode	Pollutant	Operating conditions	Organics removal efficiency	TOC removal efficiency	Metabolites	Ref.
		100 mA cm <sup>-2</sup> , V = 100 mL, $3 \text{ cm}^2$ surface area of a gas-diffusion cathode, 179 mg L <sup>-1</sup> initial organic concentration, in 0.05 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , pH 3, 6 h, 35 °C, feeding O <sub>2</sub>				(Ramírez et al. 2013)
	4-Chloro-2-methylphenol	0.55 V vs SCE, V = 300 mL, 72.7 mg L <sup>-1</sup> initial organic concentration, pH $2.70\pm0.05$ , 450 min, feeding O,		14.9%		(Hailu et al. 2016)
IrO <sub>2</sub> /RuO <sub>2</sub>	Triclosan	0.15 mA cm <sup>-2</sup> , V = 5 L, 0.29 mg L <sup>-1</sup> initial organic concentration, in 0.1 mol L <sup>-1</sup> NaOH, H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> = 40, pH 3, 100 min	100%		<ol> <li>2,4-Dichlorophenol,</li> <li>4-chloro-catechol,</li> <li>phenol, hydroquinone,</li> <li>p-benzoquinone, maleic,</li> <li>acetic, oxalic, formic acids</li> </ol>	(Methatham et al. 2014)
Irradiated electrochemical oxida	tion					
CuinS <sub>2</sub> -TiO <sub>2</sub> NT	2,4-Dichlorophenoxyacetic acid	0.5 V vs SCE, V = 60 mL, 10 mg L <sup>-1</sup> initial organic concentration, 500-W visible light source (280–2000 nm), in 0.05 mol L <sup>-1</sup> Na <sub>5</sub> SO <sub>4</sub> . 160 min	100%			(Wang et al. 2011)
Polyaniline-sensitized TiO <sub>2</sub>	Rhodamine B	0.6 V vs SCE, V = 80 mL, 20 mg L <sup>-1</sup> initial organic concentration, 6 cm <sup>2</sup> surface area of photoanode, 500-W UV light source (λ > 400 mm), 120 min	Nearly 100%			(Zhou et al. 2011)
BiVO <sub>4</sub>	2,4-Dichlorophenol	2.0 V vs. SCE, $V = 75$ mL, 10 mg L <sup>-1</sup> initial organic concentration, visible light irradiation ( $\lambda > 420$ nm), in 0.5 mol L <sup>-1</sup> Na <sub>3</sub> -SO, 5 h	> 90%		Molecular acids	(Abdi et al. 2014)
Bi <sub>2</sub> WO <sub>6</sub>	4-Chlorophenol	2.0 V, V = 100 mL, 10 mg L <sup>-1</sup> initial organic concentration, visible light irradiation $(\lambda > 400 \text{ nm})$ , in 0.5 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> , 12 h		65%		(Pablos et al. 2014)

electrostatic interaction,  $Cl^-$  were adsorbed to the anode chamber through the exchange membrane and oxidized to  $Cl_2$ ; the anode chamber also has a certain dechlorination ability to oxidize the chlorinated organic matter into molecular acids, even H<sub>2</sub>O and CO<sub>2</sub> (Xu et al. 2019). More routes are expected to be developed in the future.

An electrochemical reduction-oxidation process combines direct electrochemical reduction and electrochemical oxidation (anodic oxidation). In this process, halogenated organics are abated by direct cathodic reduction of the substrate to dehalogenated compounds, coupled with direct anodic oxidation to CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Scialdone et al. (2012b, 2012) proposed a combined process involving direct cathodic reduction at an Ag cathode and direct anodic oxidation at a BDD cathode for the degradation of halogenated organics, such as 1,2dichloroethane and Cl<sub>2</sub>HC-CHCl<sub>2</sub>. Their combined process gave higher abatement (close to 100%) of the pollutants with the same amount of passed charge, and the same applied cell voltage compared with the levels achieved by reduction and oxidation processes, respectively. This process has the benefit that the cumulative charges at the surfaces of the anode and cathode are used for pollution conversion (Scialdone et al. 2012). In the case of  $Cl_2HC$ -CHCl<sub>2</sub>, no halogenated products were detected after the electrolysis by the combined process.

Another type of indirect electrochemical reduction coupled with electrochemical oxidation for degrading halogenated organics has been thoroughly investigated by Wang's group. Their electrochemical diaphragm system consists of a Ti/ IrO<sub>2</sub>/RuO<sub>2</sub> anode and a Pd-modified carbon-based gasdiffusion electrode, e.g., Pd-modified activated carbon (Wang and Wang 2009), Pd-modified MWCNTs (Wang et al. 2012b), and Pd-modified graphene (Bian et al. 2014a; Song et al. 2017)). During electrolysis, direct anodic oxidation occurs on the surface of the Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode with electrogenerated  $MO_x(\bullet HO)$  or  $MO_{x+1}$  (Wang et al. 2012a). The graphene-based gas-diffusion cathode can produce high concentrations of H2O2 for oxidation of halogenated organic compounds (Zhang et al. 2018). In the cathode cell, the Pdmodified carbon-based gas-diffusion cathode has two functions: (i) electrocatalytic hydrodehalogenation by H<sub>abs</sub> on the Pd surface when a H<sub>2</sub> feed is supplied and (ii) cathodic indirect oxidation with electrogenerated  $H_2O_2$  by reduction of  $O_2$ when an  $O_2$  or air feed is supplied (Shi et al. 2014). The catalysts play an important role in reductive dehalogenation and acceleration of the two-electron reduction of  $O_2$  to  $H_2O_2$ . The removal efficiencies for 4-CP, 2,4-DCP, and pentachlorophenol achieved using the Pd/C gas-diffusion cathode were higher than those achieved using the C/PTFE gas-diffusion cathode (Wang and Wang 2007, 2009). When a Pd-modified activated carbon electrode was used, the removal efficiencies for CPs (4-CP, 2,4-DCP, and pentachlorophenol) reached almost 100%, and dechlorination of the three CPs exceeded 80% in 100 min (Wang et al. 2012b). The dechlorination products and the main oxidation intermediates were determined. For 4-CP, the dechlorination product was phenol, and the oxidation intermediates were hydroquinone, benzoquinone, maleic, fumaric, acrylic, malonic, oxalic, acetic, and formic acids (Wang and Wang 2007). For 2,4-DCP, the dechlorination products were 4-CP, 2-CP, and phenol, and the oxidation intermediates were hydroquinone, benzoquinone, maleic, fumaric, acrylic, malonic, oxalic, acetic, and formic acids (Wang and Wang 2008). The dechlorination product of pentachlorophenol was phenol (Wang and Wang 2009), as shown in Table 3. Shi et al. (2015) reported that the reduction of CPs by H formed by water electrolysis occurred simultaneously on the cathode surface and might compete with the reduction of  $O_2$  for electrons. This may result in a greater degree of incomplete oxidation because of stronger resistance to the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> when treating high concentrations of CPs by cathodic indirect oxidation. Xu et al. (2018b) degraded 4-BP via a combined process with a Pd-Fe/graphene catalytic cathode and a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode. The 4-BP (initial concentration  $100 \text{ mg L}^{-1}$ ) removal efficiency reached almost 100% in 60 min. Zheng et al. (2012) developed an electrolytic process involving catalytic hydrodechlorination and anodic oxidation for the remediation of groundwater contaminated by chlorinated aromatics. Note that in situ catalytic hydrodechlorination was achieved using Pd supported on bamboo charcoal in a flow-through electrolytic system with continuous generation of external H<sub>2</sub> at the cathode by water electrolysis. The sole product, i.e., phenol, was oxidized at the graphite anode. In this study, the 2,4-DCP removal efficiencies were nearly 100% at pH 2 and about 63% at pH 5.5. A low influent pH was clearly conducive to catalytic hydrodechlorination, but was not necessary.

#### **Electro-Fenton**

The EF process involves cathodic indirect oxidation combined with the Fenton process. The mechanism of EF the process is based on a free-radical chain consisting of Fe<sup>2+</sup> ions and  $H_2O_2$ , as shown in Eqs. (22)–(24) (Bach et al. 2010, Rosales et al. 2012). Unlike the case for the Fenton process,  $H_2O_2$  in the EF process is generated by two-electron cathodic reduction of oxygen gas, which is the same as the cathodic indirect oxidation process (Eq. (22)) (Burgos-Castillo et al. 2018). The strong oxidant (•OH) in this process is produced by  $H_2O_2$  activation by addition of Fe<sup>2+</sup> (Eq. (23)) (Galia et al. 2016; Gargouri et al. 2017). The halogenated organics are destroyed and converted into CO<sub>2</sub> and H<sub>2</sub>O. The removal process of halogen takes chlorine in EF as an example, the  $H_2O_2$  and •OH reacted with halogenated organics to destroy the C-Cl bond formed Cl<sup>-</sup>, and then the Cl<sup>-</sup> may be oxidized to  $Cl_2$ , or  $ClO^-$  (Burgos-Castillo et al. 2018). Note that  $Fe^{2+}$  is continuously produced in the solution via the reactions in Eqs. (24) and (25).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{22}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO' + OH^-$$
(23)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$$
(24)

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$$
(25)

Numerous experiments have been performed to compare traditional electro-oxidation and EF processes and to show the advantages of EF processes. Almost total mineralization of the original organics is obtained in the EF process, possibly because •OH is formed via two paths: anodic oxidation and a Fenton reaction between added Fe<sup>2+</sup> and electrogenerated  $H_2O_2$  in the cathodic compartment (Moreira et al. 2013). However, the contribution of anodic oxidation to the degradation is lower. For instance, Randazzo et al. (2011) investigated the synergistic action of BDD (•OH) and •OH in the bulk. In their study, 1,2-dichloroethane or Cl2HC-CHCl2 of concentration 4 mmol L<sup>-1</sup> was completely mineralized at 420 min and 300 mA by the EF process, but anodic oxidation with a Pt or BDD anode gave a poor mineralization (Randazzo et al. 2011). Many researchers have used the EF process with anodes such as BDD (Brillas et al. 2007) or graphite (Zhao et al. 2007a; Zhang et al. 2018) to enhance the degradation of halogenated organics. BDD anodes have been most studied for oxidation via the EF process of various organic pollutant, such as imidacloprid (Turabik et al. 2014), cyanazine (Borras et al. 2013), and 2,4-D (Garcia et al. 2013). Garcia et al. (2014) used electrochemical oxidation and EF process with single Pt/airdiffusion or BDD/BDD cell to degrade 2,4-D; the results were shown in Fig. 9. The 2,4-D was completely mineralized at approximately 120 min by the attack of BDD (•OH) in electrochemical oxidation with the BDD/BDD cell. The EF



**Fig. 9** Degradation of 2.5 L of 300-mg L<sup>-1</sup> 2,4-D solutions with electrolysis time in 0.05-mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> with 0.5-mol L<sup>-1</sup> Fe<sup>2+</sup>, at pH 3.0 and 35 °C. Method: ( $^{\triangle}$ ) electrochemical oxidation using BDD/BBD cell at 2.0 A, ( $\square$ ) EF with 0.5 mol L<sup>-1</sup> Fe<sup>2+</sup> using Pt/air-diffusion cell at 2.0 A, and ( $^{\diamond}$ ) EF with 0.5 mol L<sup>-1</sup> Fe<sup>2+</sup> at 2.0 A of current using coupled Pt/air-diffusion-BDD/BDD system (Garcia et al. 2014)

process with a Pt/air-diffusion cell gave complete removal in about 80 min. Figure 9 also shows that the decrease in the amount of 2,4-D was slightly more rapid when the coupled Pt/air-diffusion-BDD/BDD system was used because the oxidizing species formed in each individual cell acted simultaneously; total removal was achieved in only 60 min. Table 3 shows that Pt anodes have also been investigated for degradation of organic pollutants, such as clofibric acid (Sires et al. 2007) and 4-chloro-2-methylphenol (Hailu et al. 2016). However, the data show that the catalytic performance of the BDD anode is better than that of the Pt anode.

In addition, Methatham et al. (2014) studied the effect of operating parameters on TCS degradation by EF. In this experiment, the optimum operating conditions were found to be an operating pH of 3, an electrical current density of 0.15 mA cm<sup>-2</sup>, and a  $H_2O_2$  to Fe<sup>2+</sup> ratio of 40 for complete oxidation of 2.9 g L<sup>-1</sup> of TCS.

#### Irradiated electrochemical oxidation

Irradiated electrochemical oxidation methods, such as PEC, are emerging electrochemical advanced oxidation technology (Brillas and Martínez-Huitle 2014). The reaction mechanism of PEC with catalyst is different from that without catalyst and mainly introduces the reaction with catalyst in this review. The reaction mechanism of PEC with catalyst is light-irradiating electrode material that generates photoelectrons and holes, and the generated holes react with treated solution to form •OH, which destroyed the halogenated organic matter.

PEC oxidation is an electrochemical technique that combines electro-oxidation and photocatalysis. It degrades persistent organic pollutants (Cotillas et al. 2016; Martín de Vidales et al. 2015) and halogenated organic pollutants in wastewater by exciting an electron and a positive hole produced by incident UV/visible/solar light irradiation on a stable semiconductor anode (He et al. 2006; Philippidis et al. 2009). The positive hole can directly oxidize halogenated organic compounds, but the main function of the hole is to oxidize water to give heterogeneous •OH, which then oxidizes the organics. However, electron-hole recombination plays a major role in loss of degradation efficiency of photocatalysis. The bias potential used for the semiconductor electrode in the PEC process needs to address this issue by promoting separation of electron-hole pairs. This provides electron transfer into the external circuit and accelerates hole production, which results in efficient separation of electron-hole pairs. Many photoanode materials degrade halogenated organics well, e.g., TiO<sub>2</sub> (Bera et al. 2018; Cho et al. 2018), BDD (Martín de Vidales et al. 2016; Medeiros de Araújo et al. 2015), BiVO<sub>4</sub> (Trzesniewski et al. 2017; Shi et al. 2018), WO<sub>3</sub> (Nissen et al. 2009; Fernández-Domene et al. 2018), and  $Bi_2WO_6$  (Zhao et al. 2007b). For example, Ojani et al. (2012) reported that the results for 3,4-DCP degradation by PEC using a TiO<sub>2</sub>/graphite electrode under a potential of 1.2 V versus the reference electrode, pH 8.0, and an initial 3,4-DCP concentration of 6.7 mg L<sup>-1</sup> were better than those achieved by direct photolysis, electrochemical oxidation, and photocatalysis. Medeiros de Araújo et al. (2015) used the PEC with the BDD electrode to degrade rhodamine B (RhB) in NaCl under the current density of 90 mA cm<sup>-2</sup>; the UV irradiation wavelength is 254 nm. Also, Cotillas et al. (2018b) reported the PEC with BDD electrode total mineralization of chloramphenicol in urine under the current density of 100 mA cm<sup>-2</sup>, pH 5.6 at 25 °C.

Mainly  $TiO_2$  photoanodes have been investigated for PEC. BiVO<sub>4</sub> is a promising photoanode material for solar-driven and visible-light-driven PEC process. In this review,  $TiO_2$ and BiVO<sub>4</sub> are therefore surveyed and discussed.

 $TiO_2$  is the archetypal heterogeneous photocatalyst and is the most extensively used semiconductor electrode. It is cheap and non-toxic and has high stability and a wide band gap of 3.2 eV (Brillas and Martínez-Huitle 2014). However, TiO<sub>2</sub> has two main drawbacks: (i) low quantum yields and (ii) dominant light absorption in the UV range, which makes the process expensive (Pablos et al. 2014; Sires et al. 2014; Tang et al. 2014). Doping with metals or non-metals is an important method for improving the charge transfer rate and surface adsorption (Antony et al. 2016; Thalluri et al. 2016; Choi et al. 2017; Gutkowski et al. 2017; Wang et al. 2018b). For example, a Fe-doped TiO<sub>2</sub> film has been shown to increase the photocatalytic efficiency under visible-light irradiation compared with that of an undoped electrode (Tang et al. 2014). Many doped TiO<sub>2</sub> electrodes have been studied for enhanced photoelectrocatalysis of halogenated organics, e.g., Pt doped TiO<sub>2</sub>/Ti (Quan et al. 2004), F-TiO<sub>2</sub> (Liu et al. 2017b), and C-doped nanoparticulate TiO<sub>2</sub> (Neville et al. 2013). In addition, TiO<sub>2</sub>-based photoelectrodes have been synthesized with loaded catalysts or coupled with other semiconductors or carbon materials to improve electron-hole separation; examples are Pt/TiO<sub>2</sub> (Lakshminarasimhan et al. 2012), Co/TiO<sub>2</sub> (Liu et al. 2018a), TiO<sub>2</sub>/reduced graphene oxide (RGO)/C<sub>3</sub>N<sub>4</sub> (Ge et al. 2017), TiO<sub>2</sub>/WO<sub>3</sub> (Soares and Alves 2018; Yang et al. 2018), Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub>-S (Yan et al. 2017), Ni-doped TiO<sub>2</sub> (Dong et al. 2018), CuInS<sub>2</sub>-TiO<sub>2</sub> NT (Liu et al. 2011), RGO-Bi-TNTs (Kim et al. 2017), polyaniline (PANI)/TiO<sub>2</sub> (Wang et al. 2011), and TiO<sub>2</sub>/graphite (Ojani et al. 2012; Liu et al. 2017a). In general, these modifications for addressing the two limitations can improve the performances of TiO<sub>2</sub>-based photoanodes. For example, Liu et al. (2011) reported that the p-n heterojunction structures formed in the presence of narrow-band-gap p-type semiconductor, i.e., CuInS<sub>2</sub>, used to modify TiO<sub>2</sub> NTs, decreased electron-hole recombination, and enhanced visible-light absorption. Larger photocurrents were obtained in CuInS<sub>2</sub>-TiO<sub>2</sub> NTs when electrons from TiO<sub>2</sub> coupled with electrons captured from CuInS<sub>2</sub> and were shuttled along oriented TiO<sub>2</sub> NTs, driven by the bias voltage. This increased •OH free radical formation and enhanced the degradation efficiencies (Liu et al. 2011). A 2,4-D removal rate of 100% was achieved by using CuInS<sub>2</sub>-TiO<sub>2</sub> NTs under visible light for 160 min, the detailed data in Table 3. This is much higher than the value of 65.2% achieved with unmodified TiO<sub>2</sub> NTs. Furthermore, the 2,4-DCP degradation rate obtained in the PEC process with a PANI/TiO<sub>2</sub> film (57.5%) was higher than that achieved with pristine  $TiO_2$  (Wang et al. 2011). Chemical interactions between PANI and TiO<sub>2</sub> increased the carrier transfer efficiency and induced a synergistic effect that increased the PEC activity (Wang et al. 2011). A combination of TiO<sub>2</sub> with an adequate conductive support enables charge carrier separation and leads to enhanced conductivity of the electrode (Pablos et al. 2014). Kim et al. (2017) developed a co-doped RGO-Bi-TNTs catalyst for MB degradation; the degradation efficiency was high and the removal rate reached 93%. Figure 10 shows the PEC degradation of MB dye by single and co-doped TNT catalysts at 5 V in 150 min. The results show that the co-doped RGO-Bi-TNT catalyst (optimum three-step synthesis) gave MB removal rates 3.9, 1.5, and 1.4 times higher than those achieved with undoped TNTs, Bi-TNTs, and RGO-TNTs, respectively. The codoped sample was more efficient because both RGO and Bi enhanced the photocatalytic activity of the TNTs.

BiVO<sub>4</sub> has attracted much attention and is one of the most promising and inexpensive semiconductor materials for the degradation of halogenated organic matter. It has an excellent absorption capacity for a wide spectrum of visible light, up to 11% of the solar spectrum, because of its small band gap (only around 2.4 eV); this is smaller than that of TiO<sub>2</sub> (Zhou et al. 2011; Abdi et al. 2013). The photoactivity of the monoclinic scheelite form of BiVO<sub>4</sub> is higher than those of the tetragonal zircon form and tetragonal scheelite form (Zhou et al. 2011). Because of these features, BiVO<sub>4</sub> is expected to show excellent photoelectrocatalytic activity in halogenated organic degradation under solar light or visible light. However, BiVO<sub>4</sub>



Fig. 10 Degradation of MB under visible-light-irradiation via the PEC process (Kim et al. 2017)

photoanodes have three major drawbacks: (i) excessive surface recombination; (ii) poor charge transport; and (iii) sluggish surface oxidation kinetics (Abdi et al. 2014; Yu et al. 2017a). Many methods for resolving these issues have been investigated, such as optimizing the morphology (Liu et al. 2010), forming composite electrode (Min et al. 2014), doping (Antony et al. 2016; Thalluri et al. 2016; Gutkowski et al. 2017), and loading with electrocatalysts (Yang et al. 2013). BiVO<sub>4</sub> coupled other semiconductors and/or carbon materials to form composite electrodes would potentially provide a highly efficient photoelectrode, similar to TiO<sub>2</sub>. Heterojunction structures are formed when BiVO<sub>4</sub> is coupled with other semiconductors, e.g., WO<sub>3</sub>/BiVO<sub>4</sub> (Choi et al. 2017; Zeng et al. 2017; Xu et al. 2018c), CaFe<sub>2</sub>O<sub>4</sub>/BiVO<sub>4</sub> (Kim et al. 2014a), Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> (Cao et al. 2018), and Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> (Ju et al. 2014). These heterojunctions can decrease charge recombination on the electrode surface (Kim et al. 2014a). For example, Kim et al. (2014b) described the valence band of CaFe<sub>2</sub>O<sub>4</sub> in a CaFe<sub>2</sub>O<sub>4</sub>/BiVO<sub>4</sub> photoanode as a stepping stone for transferring holes generated from BiVO<sub>4</sub> to the electrode/electrolyte interface, leading to reduction of surface recombination and an increase in the hole injection yield. As a result, the photocurrent density obtained with the CaFe<sub>2</sub>O<sub>4</sub>/BiVO<sub>4</sub> photoanode was 65% greater than that with the bare BiVO<sub>4</sub> photoanode. Cao et al. (2018) prepared a Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> electrode and compared it with BiVO<sub>4</sub> electrodes. They found that the Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> electrode gave the best photoelectric catalytic performance. The photocurrent density increased with increasing potential. The current density of Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> electrode at the 0.5 V reached 1.25 mA  $\text{cm}^{-2}$ , which is about three times higher than that for pure BiVO<sub>4</sub> (0.31 mA cm<sup>-2</sup>). Furthermore, as shown in Fig. 11, the PEC process using Ag<sub>3</sub>PO<sub>4</sub>/BiVO<sub>4</sub> electrode gave the highest activity in norfloxacin degradation, with complete



**Fig. 11** Degradation of norfloxacin in various systems ( $C_0 = 5 \text{ mg L}^{-1}$ ; 0.5 V vs. SCE) (Cao et al. 2018)

norfloxacin degradation in 90 min ( $\lambda > 420$  nm at 0.5 V vs SCE). In comparison, the degradation of norfloxacin by PEC using BiVO<sub>4</sub> was only 61.4%, indicating that the modified Ag<sub>3</sub>PO<sub>4</sub> nanoparticles significantly improved the PEC performance of BiVO<sub>4</sub> electrodes. Furthermore, combining BiVO<sub>4</sub> with carbon materials, such as RGO and CNTs, improves electron transport. Doping of a BiVO<sub>4</sub> photoanode with metallic or non-metallic elements often increases the electronhole separation yield (Park et al. 2011). Various elements have been tested as dopants for BiVO<sub>4</sub>, such as Mo (Subramanyam et al. 2018), W (Shi et al. 2018), Bi (Wang et al. 2017), Ni (Kim et al. 2014b), Co (Kim et al. 2014b), Eu (Xue et al. 2017), and F (Xue et al. 2017). Among them, Mo or W doping of BiVO<sub>4</sub> has attracted most attention (Antony et al. 2016; Thalluri et al. 2016; Choi et al. 2017; Gutkowski et al. 2017). Doping with Mo can enhance the conductivity and increase the hole diffusion path length, resulting in a significant improvement in the photocurrent (Antony et al. 2016). Doping with W can increase the density of charge carriers, which are often responsible for the enhanced activity of doped photocatalysts, and increase electron-hole separation (Thalluri et al. 2016; Choi et al. 2017; Shi et al. 2018). According to Luo et al. (2013), the photocurrent of  $Mo^{6+}$  and  $W^{6+}$ -doped BiVO<sub>4</sub> were significantly higher than those of Sn<sup>4+</sup>-doped BiVO<sub>4</sub> and pure BiVO<sub>4</sub>. This is because of the high formation energy and lower solubility of impurity ions in Sn<sup>4+</sup>-doped BiVO<sub>4</sub>. The photocurrent of a Mo/W-codoped BiVO<sub>4</sub> photoanode was more than 10 times that of undoped BiVO<sub>4</sub> (Park et al. 2011). The photocatalytic and photoelectrocatalytic properties of electrocatalyst-loaded BiVO<sub>4</sub> are greater than those of pure BiVO<sub>4</sub>. Electrocatalysts, such as Co-based catalysts (Co<sub>3</sub>O<sub>4</sub>), RhO<sub>2</sub>, FeOOH, MnO<sub>x</sub>, PbO<sub>2</sub>, and Pd, can decrease the bias potential and improve the stability (Ding et al. 2013; Kim et al. 2014b; Shi et al. 2017) and improve the photoelectrocatalytic performance of BiVO<sub>4</sub> by decreasing the electron-hole recombination (Yang et al. 2013; Bian et al. 2014b).

Some literatures introduce the irradiation of UV light directly to electrochemical oxidation without catalysts to enhance the oxidation processes, allowing the complete mineralization of pollutants (Dos Santos et al. 2017). Malpass et al. (2012) used photo-assisted electrochemical to degrade atrazine and achieved complete degradation efficiency in 30 min. They also reported that photo-electro-Fenton process achieved good removal efficiency of atrazine. Peiter et al. (2017) used Cu<sup>2+</sup> as Fenton reagent to degrade 2,4-diclofenoxiacetic acid and obtained 54% degradation efficiency.

#### Other combined techniques

In recent years, many crafts of combined other technologies with electrochemical have emerged to reduce costs of crafts and to improve the stability of traditional biochemical treatment technology and the removal rate of halogenated organic matters. Several techniques were briefly introduced in this review.

Some recalcitrant pollutants are present in the environment for a long time and difficult to remove by conventional biological treatment techniques, such as chloronitrobenzenes (CINBs). Due to the pronounced electron-withdrawing property of the nitro and chlorine substituents on the aromatic ring, CINBs are hydrophobic and persistent, easily accumulate in the soil, and have antioxidant and antimicrobial oxidative in water, which easily affect human health through the food chain (Lin et al. 2011; Wu et al. 2006). The nature of the contaminants determines that general oxidation techniques cannot degrade them. Jiang et al. (2016) used bioelectrochemical system (BES) coupled upflow anaerobic sludge blanket (UASB) to degrade 2,4-dinitrochlorobenzene (DNCB). They found that the UASB-BES system has a good removal effect on CINBs, and the removal efficiency reached  $99.31 \pm 0.44\%$ . In this process, the biomes of UASB-BES system were remarkably more enriched, and the survival rate of organisms was higher than that of UASB. Xu et al. (2016) used microbial electrolysis cell (MEC) combined with an upflow anaerobic sludge blanket (UASB) reactor to degrade p-chloronitrobenzene, which obtained  $99.63 \pm 0.37\%$  removal efficiency. Some researchers used other combined techniques to degrade pollutants and got higher removal efficiency. For example, Peziak-Kowalska et al. (2017) proposed electrochemical oxidation or EF as pretreatment step, and biodegradation was selected as the secondary treatment method to degrade 4-chloro-2-methylphenoxy and got a good degradation efficiency. Soriano et al. (2019) used a strategy that combined membrane pre-concentration followed by electrooxidation of the concentrate to removal the persistent perfluorohexanoic acid (PFHxA). In the case of the tight nanofiltration (NF) 90 membrane used in the NF-ELOX process, the removal rate of PFHxA reached 99%, and the energy consumption was reduced by 59.2% compared to electrolysis alone. A hybrid nanofiltration/electrooxidation process is used to remove persistent PFHxA, which greatly reduces energy consumption (Soriano et al. 2017). Raschitor et al. (2017) reported a novel integrated electrodialysis/electro-oxidation (EDEO) process to degrade ionic pesticide 2,4-D, under the DSA as electrode material. They got the result which provides that the degradation rate of the EDEO to 2,4-D was more than twice that of electrochemical treatment processes in the same degradation time.

# **Conclusions and prospects**

Efficient electrochemical techniques and corresponding suitable electrode materials have been established for the degradation of halogenated organics. However, most of these techniques are still laboratory scale. Much research on the preparation and applications of suitable electrode materials together with optimization of the experimental conditions for various electrochemical techniques is ongoing. Electrochemical reduction is an effective dehalogenation treatment and avoids undesired reactions that produce toxic products or by-products. Generally, electrocatalytic hydrodehalogenation is more effective than direct electrochemical reduction. Electrochemical oxidation is an effective tool for mineralization of halogenated organics. Although emerging electrochemical oxidation processes, such as EF, PEC, and other combined techniques, give high organic removal efficiencies or TOC removal efficiencies, it is still difficult to obtain total mineralization, and undesirable toxic halogenated by-products are formed. Recent progress in emerging electrochemical reduction-oxidation processes provides an effective route for solving this problem, by removing elemental halogen by electrochemical reduction and degrading non-halogenated organics by electrochemical oxidation. This technique has great potential for the degradation of halogenated organics.

It is expected that future electrochemical technologies and combined electrochemical technologies will be widely used in industrial wastewater treatment. The future for these technologies is bright. Further research on electrode materials and their catalytic mechanisms will provide technical support for the improvement of electrochemical technology and the combined techniques. Several other complementary techniques are emerging and can provide innovative electrocatalytic materials and catalytic pathways for decontamination of effluents. We are looking forward to the development of more new joint technologies, such as the combination of ozone and electrochemical technologies.

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