

Electrochemical degradation of chlorobenzene on boron-doped diamond and platinum electrodes

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ABSTRACT

In this paper the electrochemical degradation of chlorobenzene (CB) was investigated on boron-doped diamond (BDD) and platinum (Pt) anodes, and the degradation kinetics on these two electrodes was compared. Compared with the total mineralization with a total organic carbon (TOC) removal of 85.2% in 6 h on Pt electrode, the TOC removal reached 94.3% on BDD electrode under the same operate condition. Accordingly, the mineralization current efficiency (MCE) during the mineralization on BDD electrode was higher than that on the Pt electrode. Besides TOC, the conversion of CB, the productions and decay of intermediates were also monitored. Kinetic study indicated that the decay of CB on BDD and Pt electrodes were both pseudo-first-order reactions, and the reaction rate constant (k_s) on BDD electrode was higher than that on Pt electrode. The different reaction mechanisms on the two electrodes were investigated by the variation of intermediates concentrations. Two different reaction pathways for the degradation of CB on BDD electrode and Pt electrode involving all these intermediates were proposed.

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1. Introduction

In recent decades, halogenated aromatic hydrocarbons have been introduced to the environment from a variety of sources such as pharmacy, dyeing, chemosynthesis, petroleum refining and plastics [1]. As a kind of typical harmful halogenated aromatic compound, chlorobenzene (CB) is widely found in many kinds of industrial wastewater. CB can accumulate in human body through food chain, which is obviously harmful. Cancer, teratogenesis, mutagenesis will be accordingly caused. Furthermore, it may also cause anesthetic effects and damage the central nervous system [2–4]. Moreover, CB is found to be harmful to the plants and has been listed as a prior controlled contamination by EPA.

Compared with aromatic compounds, halogenated aromatic compounds are more poisonous and more difficult to be treated by the ordinary biodegradation because of their high toxicity. Thus, it is of great importance and significance to find an efficient way to decontaminate them. Up to now, the degradation of CB was well investigated by several means, such as photocatalytic oxidation [5], Fenton oxidation [6], H_2O_2 oxidation [7], Mn catalytic oxidation [8] and ultrasonic oxidation [9]. Besides, electrochemical anodic oxidation should be taken into consideration as an effective and environmentally friendly process to cleanup the halogenated aro-

matic hydrocarbons, owing to the advantages of strong oxidability, simplicity of operation and control and high efficiency.

In aqueous system, electrochemical incineration of organic pollutants is assumed to follow two different pathways: direct oxidation at the electrode surface and indirect electrochemical oxidation mediated by appropriate formed aggressive oxidants (such as hydroxyl radicals, etc.) [10]. However, it has been reported that the hydroxyl radical ($\bullet OH$) generation ability of different anodes varies a lot, resulting in the variation of degradation performances [11,12]. Thus, it is of great importance to pursue a suitable anode for the efficient degradation.

Pt electrode is widely used in electrochemistry and catalytic chemistry for its excellent electrochemical and catalytic properties. As is known, Pt has strong ability for dehalogenation [13–18], which is helpful to the degradation of halogen aromatic hydrocarbons. However, the disadvantage of Pt is its relatively low oxygen evolution potential (ca. 1.2 V). Recently, boron-doped diamond (BDD) thin film coating on a p-Silicon substrate becomes a new electrode material, which has attracted much attention [10,19–33]. BDD electrode has the advantages of wide potential window, low background current, stable dimension and mechanical properties, exhibiting high chemical inertness and extended lifetime. Moreover, as it is known, $\bullet OH$ can be generated both on Pt and BDD electrodes, although the interaction of $\bullet OH$ with the latter was lower, causing a higher O_2 evolution potential and a higher efficiency for mineralization if enough high current (or potential) is applied, which leads to an excellent removal efficiency for organic pollutants [11]. Thus, BDD may be suitable for the application as an

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anode in the treatment of wastewater with high current efficiency and favorable TOC removal.

It has been reported that halogenated aromatic hydrocarbons could be easily dehalogenated by electrochemical reductive dehalogenation on Pt electrode and some other electrodes [34–37]. Meanwhile, the electrochemical oxidative degradation of some halogenated aromatics has also been reported [28,38,39]. However, to the best of our knowledge, intensive and comparative investigations on the electrochemical oxidation and thoroughly mineralization of CB on BDD and Pt anode has not been reported yet. The differences of the kinetics behaviors and the reaction mechanisms between the two electrodes are still not very clear.

In this paper, the electrochemical degradation of CB on BDD and Pt electrode were investigated. The formation and species of the intermediates on these two anodes were compared. Some important parameters such as reaction rate constant (k_s) and mineralization current efficiency (MCE) were also calculated, with the aim of studying the different reaction kinetics of CB degradation on BDD and Pt electrodes further. Based on these, the possible reaction pathways of the electrochemical degradation on the two anodes were also proposed.

2. Experimental

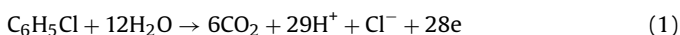
2.1. Materials

BDD (CSEM, Switzerland) was made by chemical vapor deposition on a conductive polycrystalline silicon substrate. The thickness of the obtained diamond film was about 1 μm . All the reagents were of analytical degree and purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the solutions were prepared using Double-distilled water.

2.2. Electrolysis experiments and analysis

Galvanostatic electrolyses were performed in an undivided two-electrode cell with jacketed cooler to maintain constant temperature, and the solution volume was 100 mL. The imposed current density was 5 mA cm^{-2} .

In order to avoid the volatilization of CB, and ensure the veracity of TOC measurement, the reaction cell was connected to a reflux condensing tube which was open to the atmosphere. Consecutive and circulatory water of 4 $^{\circ}\text{C}$ was used for the condensation process. The anodes were sheets of BDD or Pt with an immersed area of 5 cm^2 and the cathode was Ti foil. The gap between the anode and the cathode was 1 cm. The simulated wastewater was prepared with 170 mg L^{-1} CB solution and 0.05 M Na_2SO_4 as support electrolyte. Degradation of CB was characterized by the removal of TOC, measured on a Shimadzu TOC-VCpn analyzer. The mineralization reaction of CB can be written as follows:



The MCE at a given time t for the treated CB solution is then estimated as follows [28]:

$$\text{MCE} = \frac{\Delta(\text{TOC})_{\text{exp}}}{\Delta(\text{TOC})_{\text{theor}}} \times 100\% \quad (2)$$

where $\Delta(\text{TOC})_{\text{exp}}$ is the experimental value for TOC removal at time t and $\Delta(\text{TOC})_{\text{theor}}$ is the theoretically value of calculated TOC removal, which can be calculated as follows:

$$\Delta(\text{TOC})_{\text{theor}} = \frac{(I \times t) / (n_e \times F) \times n_c \times M \times 10^3}{V} \text{mg L}^{-1} \quad (3)$$

where I is the current intensity (A), t is electrolysis time (s), F is Faraday constant, $F = 96,485 \text{ C mol}^{-1}$, n_e is the electron transfer number in Eq. (1), n_c is the carbon number of the organic compound, M is

carbon atomic weight, $M = 12 \text{ g mol}^{-1}$, and V is the volume of the sample solution (L). For CB, n_e and n_c are 28 and 6, respectively.

Intermediate products were detected by high performance liquid chromatogram (HPLC) (Agilent HP 1100, Agilent, USA). The organic acid intermediates were detected with an AQ C18 column with phosphate buffer (pH 2.3) as the mobile phase at a flow rate of 1 mL min^{-1} . The benzenoid compound intermediates were detected with a phenyl column with 50% water/50% methanol as the mobile phase at a flow rate of 1 mL min^{-1} . The concentrations of Cl^- in the solution produced during the reactions were detected by a Cl^- selective electrode.

Assuming the formation and decay of each intermediate were pseudo first-order reaction, the formation reaction rate constant k_f and decay reaction rate constant k_d followed relation (4):

$$C_i = \frac{k_f C_0}{k_d - k_f} (e^{-k_f t} - e^{-k_d t}) \quad (4)$$

where C_i is the intermediate concentration, C_0 is the concentration of initial reactant, k_f and k_d is the formation and decay reaction rate constant, respectively. Genetic algorithm [40], as a promising stochastic optimization method, was used to fit the data to determine k_f and k_d .

The percentage of CB converted into CO_2 , relative to the amount of degraded CB, could be calculated from the values of TOC using the relation:

$$\% \text{CO}_2 = \frac{\{[\text{TOC}]_0 - [\text{TOC}]_t\} / 6}{[\text{CB}]_0 - [\text{CB}]_t} \times 100 \quad (5)$$

where $[\text{TOC}]_0$ and $[\text{TOC}]_t$ are the TOC at time 0 and t (in mM), respectively, $[\text{CB}]_0$ and $[\text{CB}]_t$ are the concentrations of CB at time 0 and t (in mM), respectively.

The term $\{[\text{TOC}]_0 - [\text{TOC}]_t\} / 6$ represents the mole number of phenol converted into CO_2 [41].

The percentage of CB converted into aromatic intermediates, relative to the amount of degraded CB, has been defined as:

$$\% \text{Aromatics} = \frac{[\text{Aromatics}]}{[\text{CB}]_0 - [\text{CB}]_t} \times 100 \quad (6)$$

where [Aromatics] is the concentration of aromatic intermediates (*p*-benzoquinone, 1,4-dihydroxybenzene, 1,2-dihydroxybenzene, 1,3-dihydroxybenzene and chlorophenol) in mM.

The percentage of CB converted into acid intermediates, relative to the amount of degraded CB, has been defined as:

$$\% \text{Acids} = \frac{[\text{Acids}]}{[\text{CB}]_0 - [\text{CB}]_t} \times 100 \quad (7)$$

where [Acids] is the concentration of CB converted into acid intermediates (maleic acid, oxalic acid and formic acid) in mM.

2.3. Electrochemical measurement

Cyclic voltammetry (CV) was carried out in a typical three-electrode system on a CHI760B electrochemical workstation (CH Instruments, USA). BDD or Pt was used as the working electrode, saturated calomel electrode (SCE) as the reference electrode and Ti as the counter electrode. All measurements were performed at the room temperature ($20 \pm 2^{\circ}\text{C}$).

3. Results and discussion

3.1. Oxidation behavior of CB on BDD and Pt electrodes

CV method was first used to study the oxidation behavior of CB on BDD and Pt electrodes. Fig. 1A shows the CV curves recorded at 50 mV s^{-1} scan rate in 0.05 M Na_2SO_4 solution containing 1.5 mM

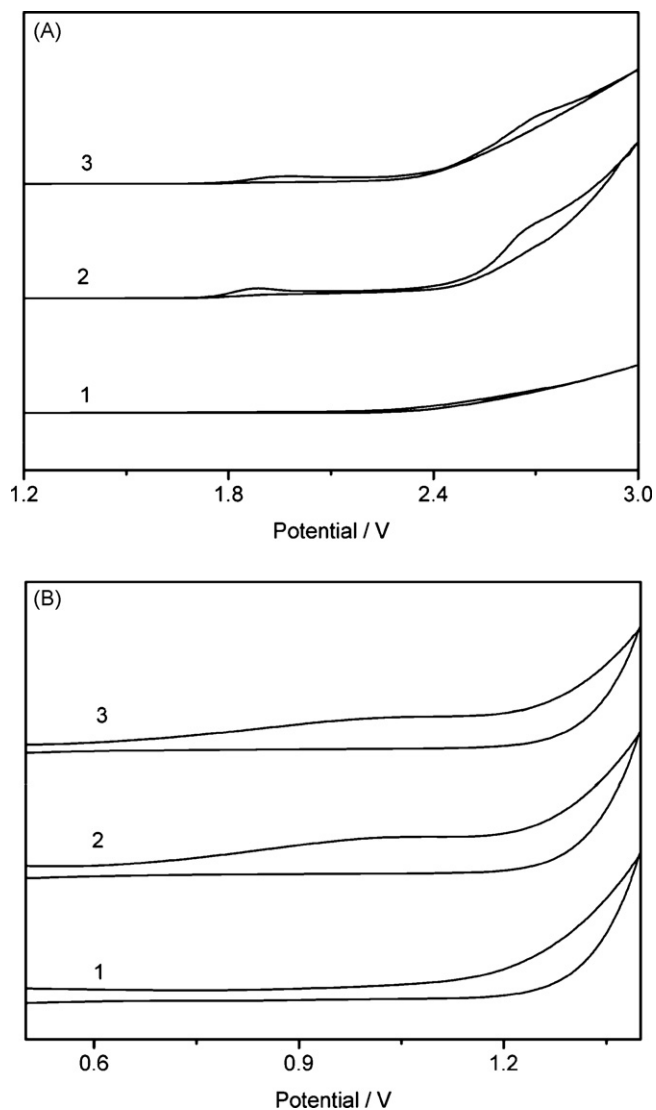


Fig. 1. (A) CV responses of BDD in 0.05 M Na₂SO₄ solution (1: blank; 2: with CB; 3: with benzene). (B) CV responses of Pt in 0.05 M Na₂SO₄ solution (1: blank; 2: with CB; 3: with benzene).

CB. As shown in Fig. 1A (curve 2), CB could be electrochemical oxidized on BDD. Two anodic peaks could be observed in the potential range from 1.89 V to 2.66 V and no cathodic peak was observed, indicating that the oxidation of CB on BDD electrode was irreversible. The CV response on Pt electrode was different from that on BDD. As shown in Fig. 1B (curve 2), only one anodic peak located at 1.02 V was observed for CB oxidation, while no cathodic peak could be observed, indicating that the oxidation of CB on Pt electrode was also irreversible. To further study the impact of chlorine substitute on the oxidation behavior of CB on BDD, CV of benzene was carried out for comparison. Curve 3 in Fig. 1A and curve 3 in Fig. 1B presented the CV response of benzene on BDD and Pt, respectively. Similarly, two anodic peaks of benzene on BDD could also be observed. However, the potentials of these two anodic peaks were 1.94 V and 2.69 V, which were higher than those of CB. It was assumed that the anodic peak at 1.89 V was caused by the oxidation of the hydrogen in the benzene ring and the one at 2.66 V was caused by the benzene ring cleavage. Furthermore, with the effect of chlorine in the benzene ring, the potentials of these two anodic peaks of CB were lower than those of benzene. Similarly, the oxidation processes of CB and benzene were irreversible since neither of them was observed to have cathodic peaks.

However, the CV response of benzene on Pt electrode was almost the same as that of CB (Fig. 1B), indicating that the oxidation behavior of CB on Pt electrode was the same as that of benzene. The anodic peak at 1.02 V can be attributed to the reaction of benzene ring instead of the reaction of chlorine. It was assumed that because of its relatively low oxygen evolution potential, the anodic peak at 2.06 V caused by the benzene ring cleavage reaction could not be observed on Pt.

Moreover, oxygen evolution potential is an important parameter of the electrode which influences the degradation efficiency of organic compounds. Experiment result showed that the oxygen evolution potential of BDD electrode in 0.05 M Na₂SO₄ solution was 2.1 V, much higher than the 1.2 V on Pt electrode, which may be related to the different •OH generation ability of these two electrodes. As it is known, most of the electrochemical oxidation processes on the anode are reported to be mediated and performed via •OH or other active intermediates that are produced on the anode surface by the discharge of water or electrolyte [10]. •OH can be produced both on Pt and BDD electrodes, although the interaction of •OH with the latter was lower, causing a higher O₂ evolution potential. Accordingly, a greater efficiency for mineralization leads to a higher removal efficiency for organic pollutants [11].

On the other hand, the chlorine in the CB may be converted to Cl⁻ and further oxidized. Thus, the evolution potential of Cl should also be considered. Electrochemical experiments indicated that the Cl₂ evolution potential in 0.05 M Na₂SO₄ containing 1.5 mM Cl⁻ were 2.0 V and 0.9 V on BDD and Pt, respectively. This result indicated that Cl⁻ was more easily to be oxidized on Pt than on BDD.

3.2. CB degradation and TOC removal on BDD and Pt electrodes

In order to study the degradation of CB on BDD and Pt electrode, galvanostatic electrolysis was carried out with a current density of 5 mA cm⁻². TOC of the solution during the electrolysis was successively monitored and MCE was calculated according to Eq. (2). Experiment result showed that under such a low current density, the electrode potentials (vs. SCE in three electrode system) were 4.8 V and 2.2 V on BDD and Pt, respectively, which were still higher than their O₂ evolution potentials (2.1 V and 1.2 V for BDD and Pt, respectively). Thus, indirect oxidation would be the dominating process [31]. CB and the intermediates were oxidized mainly by •OH, which were produced on the surfaces of the anodes. However, as mentioned above, the production performance of •OH on Pt and BDD electrodes were different. •OH showed lower interaction on the surface of BDD, which causes a higher O₂ evolution potential. Thus, BDD may exhibit better MCE, TOC removal and faster oxidation rate for the degradation of CB compared with Pt.

However, it must be noted that whatever on BDD or Pt, water decomposition cannot be avoided when the electrode potentials are higher than O₂ evolution potentials. The higher the electrode potential is, the more severe the decomposition takes place. Therefore, the current density of 5 mA cm⁻² was applied in our work to achieve relatively high MCE.

Fig. 2A shows the variation of CB concentration along with electrolysis time on BDD or Pt anode. The CB concentration decreased faster on BDD than on Pt electrode. Kinetic calculation showed that the decay of CB on BDD and Pt anode were both pseudo-first-order reactions (see the inset of Fig. 2A) and the reaction rate constant *k* was 1.97 × 10⁻⁴ s⁻¹ on BDD and 1.25 × 10⁻⁴ s⁻¹ on Pt, respectively.

Fig. 2B shows that TOC in the solution could be quickly removed with a current density of 5 mA cm⁻² on BDD anode and the removal of TOC reached 94.5% after 6-h degradation. Under the same experimental condition, the removal was only 85.2% on Pt anode. After 8 h, the TOC removal gradually reached 90.3% by using Pt anode, which was still lower than the value of 6-h degradation on BDD.

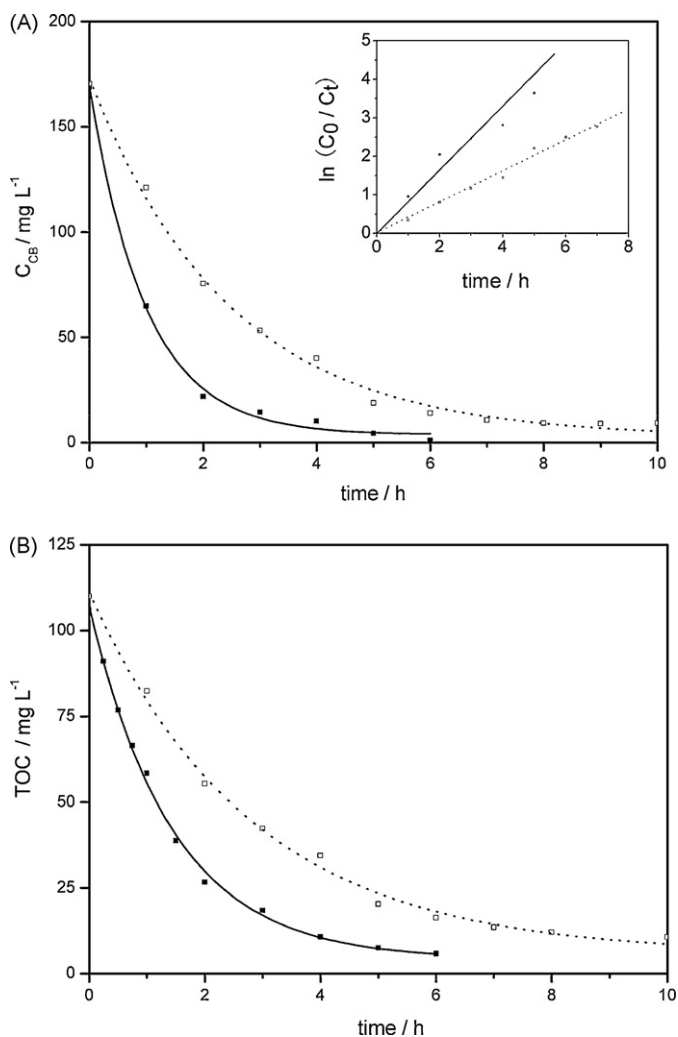


Fig. 2. (A) CB concentration decay with electrolysis time during the electrolysis of 170 mg L^{-1} CB in 0.05 M Na_2SO_4 with a BDD (—■—) or Pt (··□··) anode. Inset: The kinetic analysis assuming a pseudo-first-order reaction for CB concentration decay. (B) TOC decay with electrolysis time with a BDD (—■—) or Pt (··□··) anode.

Furthermore, based on the TOC values, MCE of CB on BDD and Pt was calculated. During the degradation, MCE of BDD was approximately 100% in 1-h electrolysis. As the oxidation reaction went on, the concentrations of the contaminations decreased. Meanwhile, the possibility of water decomposition increased, resulting in the gradual decline of MCE. As for Pt, it was only 91% under the same condition in 1-h electrolysis, and declined subsequently. It could be noticed that due to the influence of the reactant consumption and the side reaction (H_2O oxidation), MCE of both BDD and Pt anode decreased. Nonetheless, MCE of BDD was higher than that of Pt all the while.

3.3. Kinetic study of the degradation reaction

From Fig. 2A and B, it could be observed that the TOC decay efficiency was lower than that of CB decay during the electrolysis on BDD and Pt electrodes. This phenomenon indicated that some intermediates were generated during the electrolysis process. Thereby, it was necessary to analyze the components of these intermediates.

First, the concentration of Cl^- in the solution during the electrolysis process was determined by Cl^- selective electrode. Fig. 3 shows the variation of Cl^- concentrations. The variation of Cl^- con-

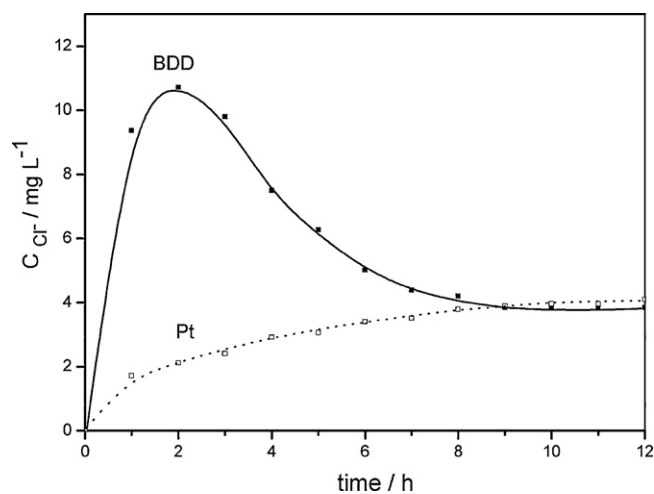


Fig. 3. Evolution of Cl^- concentration during electrolysis with a BDD (—■—) or Pt (··□··).

centrations on BDD electrode was rather different from that on Pt electrode. On BDD electrode, the Cl^- concentration reached a peak value of 10.7 mg L^{-1} after 2 h oxidation. Then it decreased and reached the value of 3.8 mg L^{-1} after 10 h. This concentration value did not change evidently after 10 h oxidation. However, when using a Pt electrode, Cl^- concentration increased slowly and reached 4.1 mg L^{-1} in 10 h, and then the concentration did not change obviously.

It was reported that Pt exhibited good dehalogenation ability [13–17]. When Pt was used as anode for the electrochemical degradation of CB, the concentration of Cl^- remained at a relatively low level during the whole process. It was presumed that it could be attributed to two reasons. On the one hand, compared with BDD, the decay rate of CB on Pt was slower ($k = 1.25 \times 10^{-4} \text{ s}^{-1}$), resulting in a relevant low production of Cl^- . On the other hand, on Pt electrode, Cl substitute of the decayed CB could be dechlorinated quickly from the benzene ring as Cl^- , and it was much easier for Cl^- to be further oxidized subsequently. Contrarily, on BDD electrode, the decay of CB was rapid. In the initial period, abundant Cl^- came into the solution. However, Cl_2 evolution potential on BDD was relatively high, which result in a slower oxidation rate of Cl^- . Thus, the concentration of Cl^- accumulated to a peak value. As the reaction went on, CB was oxidized continuously, with the concentration of CB decreased. Meanwhile, Cl^- was also oxidized slowly, with the detected concentration gradually declined.

HPLC was applied to identify other intermediates and their concentrations were also determined. The intermediates produced during the degradation could be classified as benzenoid intermediates and organic acids intermediates. Thus, they were detected with a phenyl column and an AQ C18 column, respectively.

Results indicated that most of the intermediates were the same on both electrodes except the following differences. First, 4-chlorophenol was detected on BDD electrode but was not detected on Pt electrode. Contrary, 1,3-dihydroxybenzene was detected on Pt electrode but was not detected on BDD electrode. This phenomenon also proved that Pt exhibited better dechlorination ability than BDD. Therefore, when $\cdot\text{OH}$ attacked CB, it was easier for CB to be dechlorinated simultaneously on Pt. Thus, nearly no 4-chlorophenol was produced but several kinds of dihydroxybenzenes were detected. Contrarily, when $\cdot\text{OH}$ attacked CB on BDD, CB might only be partially dechlorinated. Thus, 4-chlorophenol and dihydroxybenzenes could both be detected during the degradation process. Second, the concentration conversion of each intermediate was not the same during the electrolysis on BDD electrode and Pt electrode. Fig. 4

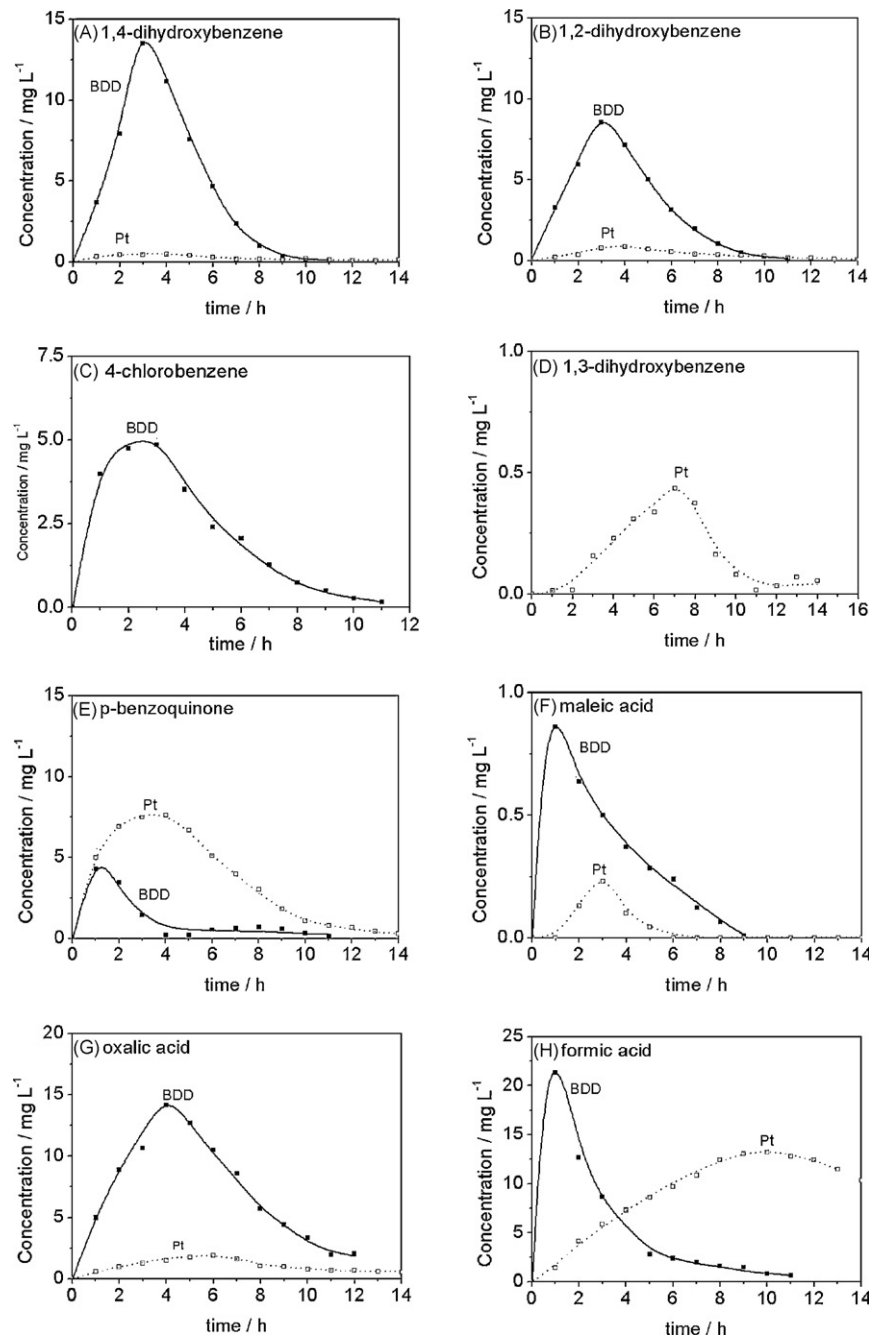


Fig. 4. Concentration evolution of each intermediate during the electrolysis on BDD (—■—) and Pt (••□••).

compared the concentration variation of each intermediate during the electrolysis on the two electrodes. The concentrations of 1, 4-dihydroxybenzene, 1, 2-dihydroxybenzene, maleic acid and oxalic acid on BDD electrode were higher than those on Pt electrode. However, the concentration of *p*-benzoquinone on Pt electrode was higher than that on BDD electrode. Nevertheless, these intermediates were mineralized ultimately on both electrodes. In addition, remarkable differences of formic acid concentration between the BDD and Pt electrode could be observed. During the electrolysis on BDD electrode, the concentration of formic acid reached a peak value in 1.2 h and then mineralized thoroughly in 8 h. While on Pt electrode, the concentration of formic acid reached its peak value in 10 h, and then decayed slowly without thoroughly mineralization at least in 14 h. Moreover, the peak value of formic acid concentra-

tion on BDD electrode was a little higher than that on Pt electrode. Table 1 listed the intermediates maximum concentration (C_{\max}) and their corresponding accumulation time (τ_{\max}) on BDD and Pt electrodes.

Table 2 presented the k_f and k_d of each intermediate during the electrolysis of CB on BDD and Pt according to Eq. (4). k_f and k_d are obviously different, which leads to the differences in the concentration of each intermediate.

Furthermore, according to the concentrations of intermediates on BDD and Pt electrode, the percentages of decayed CB converted into CO_2 , aromatic intermediates and acids, respectively were calculated following Eqs. (5)–(7). These results were showed in Fig. 5. It can be observed from Fig. 5 that the conversion of decayed CB on BDD and Pt was different. During the electrolysis, the percent-

Table 1

The intermediate's accumulative maximum concentration (C_{\max}) and their corresponding time (τ_{\max}) during electrolysis of CB on BDD and Pt electrode.

	C_{\max} (mg L ⁻¹)		τ_{\max} (h)	
	BDD	Pt	BDD	Pt
1,4-Dihydroxybenzene	13.53	0.49	3.00	3.72
1,2-Dihydroxybenzene	8.51	0.84	3.10	3.99
1,3-Dihydroxybenzene	/	0.43	/	7.03
Chlorophenol	4.95	/	2.64	/
<i>p</i> -Benzoquinone	4.43	7.54	1.20	3.61
Oxalic acid	14.16	1.86	4.00	5.99
Maleic acid	0.90	0.22	0.99	3.00
Formic acid	21.42	13.15	1.20	10.0

Table 2

k_f and k_d of each intermediate during the electrolysis of CB on BDD and Pt electrode.

	k_f (s ⁻¹)		k_d (s ⁻¹)	
	BDD	Pt	BDD	Pt
1,4-Dihydroxybenzene	4.44×10^{-5}	2.61×10^{-5}	6.36×10^{-4}	9.08×10^{-3}
1,2-Dihydroxybenzene	4.44×10^{-5}	8.33×10^{-7}	9.44×10^{-4}	2.86×10^{-4}
1,3-Dihydroxybenzene	/	1.61×10^{-7}	/	9.17×10^{-5}
Chlorophenol	5.83×10^{-5}	/	1.79×10^{-3}	/
<i>p</i> -Benzoquinone	1.41×10^{-4}	3.06×10^{-5}	3.23×10^{-3}	5.81×10^{-4}
Oxalic acid	4.44×10^{-5}	8.33×10^{-7}	1.64×10^{-4}	2.14×10^{-4}
Maleic acid	8.61×10^{-5}	2.22×10^{-5}	1.90×10^{-2}	2.48×10^{-2}
Formic acid	1.17×10^{-4}	1.39×10^{-6}	1.65×10^{-3}	3.06×10^{-5}

age of CB converted into aromatic intermediates on BDD (curve 3 in Fig. 5) was higher than that on Pt (curve 4 in Fig. 5). This phenomenon indicated that the cleavage reaction of benzene ring took place at a lower potential on Pt electrode than that on BDD, which could probably be attributed to the catalytic dehalogenation performance of Pt. The percentage of CB converted into acids on BDD (curve 5 in Fig. 5) reached the peak value in 1 h and then decreased rapidly. Contrarily, the percentage of CB converted into acids on Pt (curve 6 in Fig. 5) increased slowly and reached the same value as that on BDD in 6 h, and then increased continuously. In the initial 2 h, the percentage of CB converted into CO₂ on Pt (curve 2 in Fig. 5) was higher than that on BDD (curve 1 in Fig. 5), but after 6 h this percentage on BDD was higher than that on Pt.

According to the concentration conversion of intermediates during the electrolysis, the pathway of the electrochemical degradation of CB on BDD and Pt anodes could be proposed. Fig. 6 showed the supposed pathways on these two anodes.

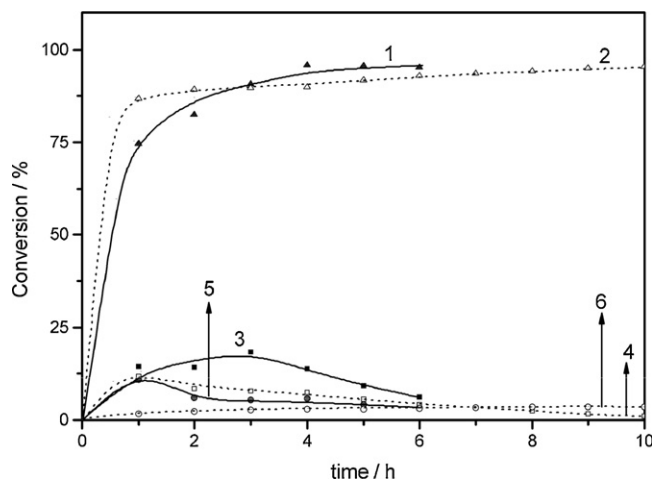


Fig. 5. Trend of the percentage of decayed CB converted to CO₂, aromatic compounds and acids during electrolysis on BDD or Pt. (1: CO₂% on BDD; 2: CO₂% on Pt; 3: aromatics% on BDD; 4: aromatics% on Pt; 5: acids% on BDD; 6: acids% on Pt).

The intermediates could be classified into two categories: benzenoid compounds and organic acids. The formation and decay of the intermediates could be divided into two stages. Take the cleavage of benzene ring as separation, the formation of phenols and *p*-benzoquinone before it could be regarded as the first stage. Meanwhile, the consequent conversion of oxalic acid, formic acid and maleic acid could be the second stage.

Thus, in the first stage, •OH attacked the benzene ring, 4-chlorophenol and dihydroxybenzenes formed on BDD. As for Pt, because of its good dechlorination performance, only dihydroxybenzenes formed. Subsequently, phenols were all oxidized to benzoquinone. In the second stage, benzoquinone converted to maleic acid, which further converted to oxalic acid, formic acid. And finally, they were thoroughly mineralized.

Furthermore, according to the concentrations showed in Fig. 4, the average molar percentage of each intermediate in each stage could be calculated. In the first stage, the main intermediate was phenols on BDD with an average molar percentage of 83%, while on Pt it was *p*-benzoquinone with an average molar percentage of 77%. In the second stage, the main intermediates were formic acid (47%) and oxalic acid (50%) on BDD, and formic acid (93%) on Pt, respectively. Based on these calculations, the main intermediates of each stage were highlighted by dashed line frame in Fig. 6.

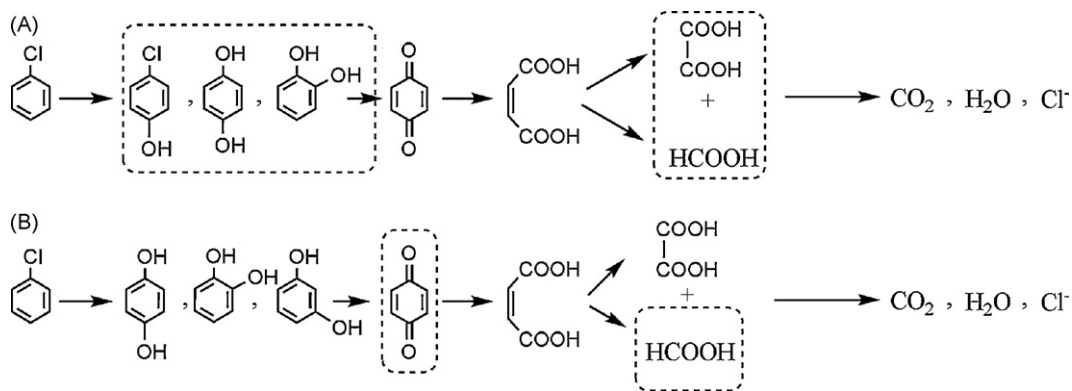


Fig. 6. Proposed reaction sequence for CB degradation by anodic oxidation with a BDD (A) or a Pt (B) electrode. The intermediates with dashed line frame were main intermediates of each stage.

4. Conclusion

In this work, the electrochemical degradation of CB solution on BDD and Pt electrode was investigated for comparison. The TOC removal, MCE and reaction kinetics of these two electrodes were investigated. In the degradation process, CB could be thoroughly mineralized on BDD electrode. At a current density of 5 mA cm^{-2} and an electrode area of 5 cm^2 , the TOC removal reached 94.5% in 6 h on BDD electrode. But under the same condition, the TOC removal was only 90.3% in 8 h on Pt electrode. Experimental result proved that the calculated MCE on BDD anode was higher than that on Pt anode. Thus, as an ideal anode, BDD electrode was more suitable for the electrochemical mineralization of CB than Pt electrode when energy consumption was taken into account.

The reaction kinetics and reaction mechanisms of CB on BDD electrode and Pt electrode were also studied by investigating the variation of each intermediate's concentration during the electrolysis. During the electrolysis on BDD and Pt electrode, most of the intermediates were the same. However, on BDD electrode 4-chlorophenol was detected. While on Pt electrode, it could not be detected. The concentration difference of each intermediate indicated different reaction rate constant and pathway. Furthermore, the concentration of Cl^- during the electrolysis on Pt electrode was lower than that on BDD electrode owing to its lower Cl_2 evolution potential and favorable dechlorination performance.

These results demonstrated that although Pt electrode had its advantage in catalytic dechlorination, BDD electrode was more suitable for the total mineralization of CB with the advantages of higher TOC removal, better MCE and eco-friendly characteristic. Thus, BDD could be an ideal anode for the electrochemical degradation of halogen aromatic contaminations.

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