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Electrochemical Oxidation of 1,4-Dichlorobenzene on Platinum Electrodes in Acetonitrile-Water Solution: Evidence for Direct and Indirect Electrochemical Oxidation Pathways

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The degradation of 1,4-dichlorobenzene (*p*-DCB) in acetonitrile-water solution was investigated under electrochemical oxidation on a platinum electrode. The related mechanism was proposed through the organic analysis and electrochemical measurements such as chronoamperometric and cyclic voltammetric measurements. The cyclic voltammogram curves of *p*-DCB, parachlorophenol, parahydroquinone, 2,5-dichlorophenol , and 2,5-dichlorohydroquinone showed two oxidation peaks (1.8, 2.3 V (vs SCE)), (1.1, 1.9 V (vs SCE)), (0.7, 1.8 V (vs SCE)), (1.1, 2.2 V (vs SCE)), and (0.7, 1.8 V (vs SCE)), respectively. The oxidation peaks of 1,4-benzoquinone and 2,5-dichloro-*p*-benzoquinone were found at the potential of 1.8 (vs SCE), coinciding with the oxidation potential of platinum. The results of cyclic voltammetric and chronoamporometric experiments suggested that both direct and indirect electrochemical oxidation processes involved the degradation of *p*-DCB. For the intermediates, 1,4-benzoquinone and 2,5-dichloro-*p*-benzoquinone underwent indirect oxidation, parahydroquinone and 2,5-dichlorohydroquinone degraded mainly by direct oxidation, and parachlorophenol and 2,5-dichlorophenol removed by both direct and indirect oxidation. Furthermore, a possible degradation scheme for the oxidation of *p*-DCB in acetonitrile-water solution was proposed.

Keywords: Pt electrode, mechanism, 1,4-dichlorobenzene, anodic oxidation, direct electrochemical oxidation

1. INTRODUCTION

Chlorinated benzenes (CBs), which can enter the aquatic environment as solvents, and by-product materials of phenol and pesticide manufacturing, are ubiquitous due to their widespread use during the past decades [1]. Because of the high toxicity and low biodegradation properties, the presence and accumulation of these substances in aquatic systems and biological organisms pose a severe toxicological risk [2, 3]. Therefore, it is highly desirable to develop efficient technology for the degradation of CBs.

Various methods such as biodegradation [4-6], adsorption [7, 8], incineration [9, 10], catalytic hydrodechlorination [11], and photocatalysis [12] have been applied to the degradation of CBs in wastewater.

Recently, electrochemical oxidation is suggested as a very promising approach method [13]. This method offers some advantage such as the environmental compatibility, and amenability to automation. For these reasons, environmental scientists have been concentrating on the destruction of CBs by electrochemical oxidation [14]. Among the different anodic materials, platinum (Pt) finds extensive application as electrode materials in electrochemical industries due to its good electrocatalytic activity, and chemical stability even at high potentials [15]. As is known, Pt electrode has also been used for oxidation of various CBs such as chlorobenzene [16], and 1,4-dichlorobenzene (*p*-DCB) [17] etc.

From the mechanism point of view, electrochemical oxidation for the organic pollutants can be removed by (i) direct electrolysis (pollutants exchange electrons directly with the anode surface), or (ii) indirect electrolysis (compounds oxidized through the mediation of some electroactive species regenerated there) [18-20]. The electrochemical oxidation mechanism of the compounds have been investigated through the method of organic analysis [21]. The advantage lies in the qualitative and quantitative analysis of the intermediate products. However, these studies could not provide sufficient direct evidences to support the proposed mechanism. Whether the intermediate products are further removed by direct or indirect oxidation process, which can be generally illuminated by chronoamperometric and cyclic voltammetric (CV) measurements. The literatures report that the degradation of phenol due to direct oxidation and hydroxyl radical mediated oxidation is quantified by chronoamperometry measurements [19]. Surprisingly, so far, a combination of the two methods has not been reported in the electrochemical oxidation mechanism of CBs. In fact, these methods could extensively explore the reaction mechanism.

Herein, *p*-DCB is chosen as a representative of CBs since it is one kind of the toxic organic compounds listed by Environmental Protection Agency as priority pollutants [22]. Additionally, CBs mainly exist in chemical industry wastewater and often mix with the organic and water solutions [23-25]. Recent studies have focused on the degradation of CBs in organic [26] or water solution [27]. However, the investigation of the CBs in mixture solution is rarely reported. In fact, the degradation of the CBs in mixture solution is more important than that in pure water in view of practical application. In this study, a new methodology is developed by combining organic analysis, chronoamperometric measurements, and CV measurements that could effectively elucidate the electrochemical oxidation mechanism of *p*-DCB on Pt electrode in acetonitrile-water solution. We believe that investigation on the mechanism of electrochemical oxidation will be worthy of further application.

2. EXPERMENTAL

2.1. Reagents

2,5-dichlorophenol, 2,5-dichlorohydroquinone and 2,5-dichloro-*p*-benzoquinone were purchased from Sigma Chemical Company (USA). All the other chemicals, including acetonitrile, *p*-DCB, parachlorophenol, 1,4-benzoquinone, parahydroquinone, and sodium perchlorate, were analytical grade and purchased from Huadong Medicine Hangzhou Co. Ltd., Hangzhou, China. All the other chemicals were used without further purification, and doubly distilled water was used throughout.

2.2. Characterization of the electrode

The surface morphology of the electrodes was characterized by scanning electron microscopy (SEM, Hitachi S-4700 II). The morphology of the surface, after electrolysis the Pt anode at 2.3 V (vs saturated calomel electrode (SCE)) in the 2,5-dichlorophenol solution, was shown in Figure 1. It could be seen the polymer film, which was clearly identified as a rough surface in comparison to a clean and flat surface of the Pt electrode without polymer film.

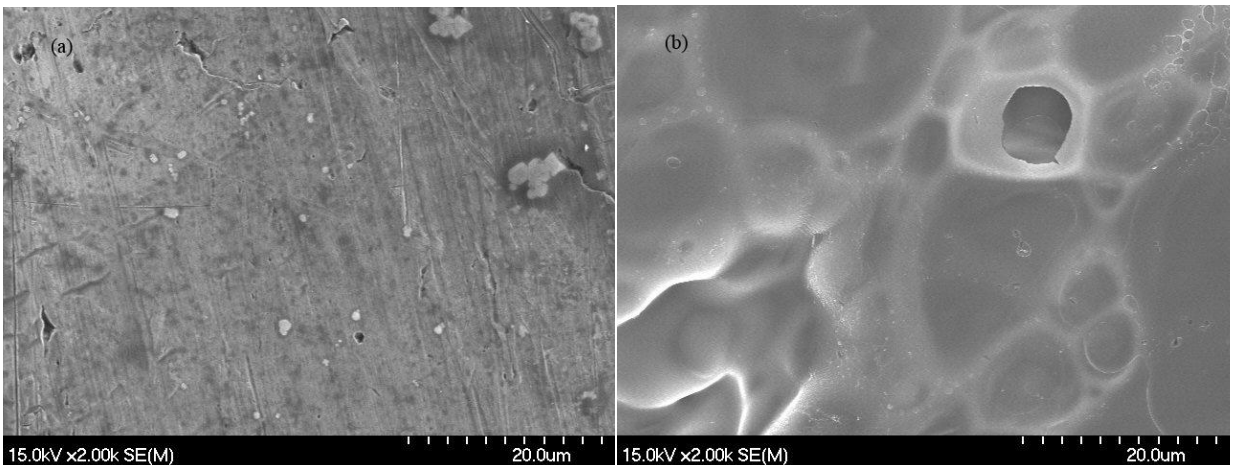


Figure 1. SEM image of the Pt electrode displaying the surface of electropolymerized film of 2,5-dichlorophenol (a) before electrolysis, and (b) after electrolysis at 2.3 V (vs SCE) for 0.5 h.

2.3. Electrochemical measurements

CV and chronoamperometric measurements were performed in a conventional three-electrode cell made of pyrex glass with a PAR 2273 potentiostat (Princeton Applied Research, USA). The solvents were mixture of doubly distilled water and acetonitrile (v:v, 50:50), with 0.1 M $NaClO_4$ as the supporting electrolyte. The three-electrode system consisted of a Pt electrode (2×2.5 cm^2) as an auxiliary electrode, SCE as a reference electrode, and the 0.5 mm diameter Pt disk electrode sealed in a glass tube as a working electrode. All electrochemical measurements were performed at 25±1 °C.

2.4. Bulk electrolysis

The detailed procedures for the scheme of the experimental setup had been described [17]. Electrochemical oxidation of *p*-DCB and 2,5-dichlorophenol were done in a diaphragm three-electrode cell, respectively.

2.5. Analytical methods

The concentration of *p*-DCB and its degradation products in electrolyzed solutions were monitored with an Agilent 1200 Series high-pressure liquid chromatography system (HPLC) with an Eclipse XDBC-18 column (150 mm × 4.6 mm, 5 μm film thickness) and a DAD detector. The column temperature was 30 °C. The concentration of *p*-DCB and its degradation was determined by HPLC at a flow rate of 0.8 ml/min with a step gradient [17], and identified by DAD and ESI-MS (Agilent 6210 LC/TOF-MS).

Formate, acetate, oxalate, malcate, and chloride ions produced during electrolysis were analyzed with a Dionex model ICS 2000 ion chromatograph (IC) equipped with a dual-piston pump, a Diones IonPac AS19 analytical column (4 mm × 250 mm), an IonPac AG19 guard column (4 mm × 250 mm), and a Dionex DS6 conductivity detector. Suppression of the eluent was achieved with a Dionex anion ASRS electrolytic suppressor (4 mm) in the autosuppression external water mode.

3. RESULTS AND DISCUSSION

3.1. Evolution of p-DCB by electrochemical oxidation

In order to achieve the information required to elucidate the oxidative mechanism of *p*-DCB, an analysis of the solution composition obtained after electrolysis at 2h on Pt electrode (2.3 V (vs SCE)), was investigated by HPLC, HPLC/MS, and IC.

The IC chromatogram result was shown in Figure 2(a). Five peaks were classified by comparing the retention time of formate, acetate, chloride, malcate, and oxalate standard solution. The compounds were detected at the retention time of 4.7 min (peak 1 in Figure 2(b)), 5.2 min (peak 2 in Figure 2(b)), 6.8 min (peak 3 in Figure 2(b)), 13.3 min (peak 4 in Figure 2(b)), and 13.7 min (peak 5 in Figure 2(b)) which were eluted at the comparable retention time as peak 1, peak 2, peak 3, peak 4, and peak 5 (Figure 2(a)), respectively.

The Figure 3(a) was applied to analyze the sample solution of 1,4-benzoquinone, parachlorophenol, 2,5-dichloro-*p*-benzoquinone, and 1,4-dichlorobenzene by HPLC. Four major chemicals were separated satisfactorily.

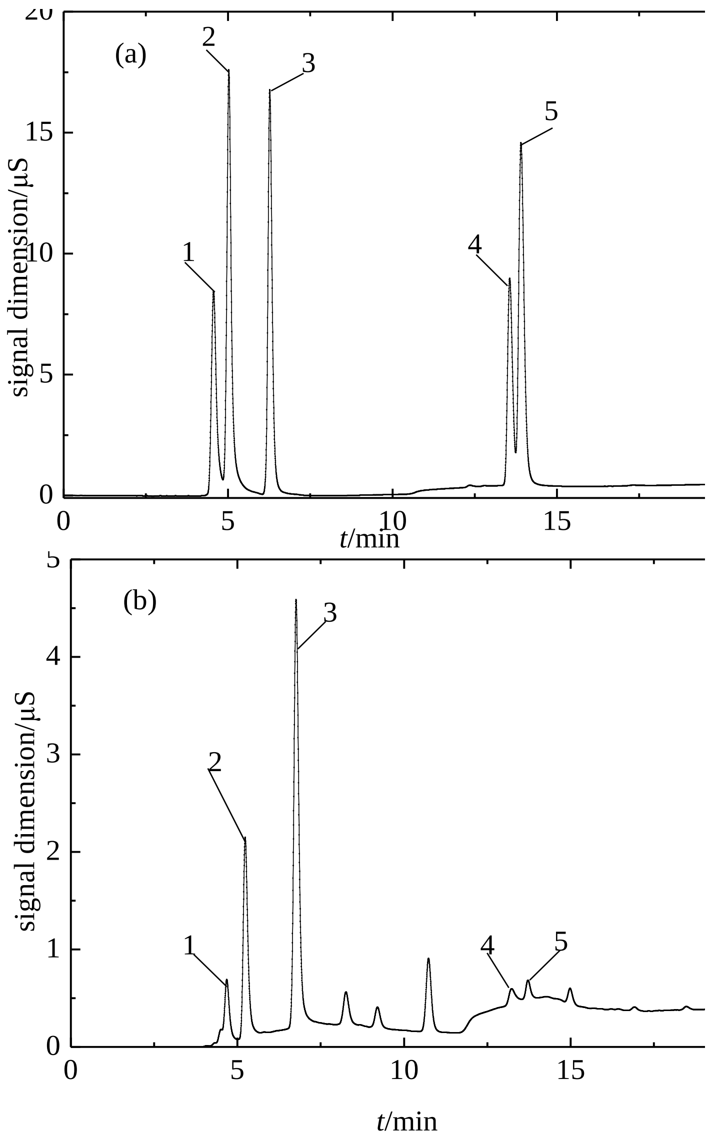


Figure 2. IC chromatogram of the small organic acids in different combination of solution Note: (a). standard mixture, (b). the intermediate products formed in the electrochemical oxidation degradation of *p*-DCB at 2h; 1. formate, 2. acetate, 3. chloride, 4. malcate, 5. oxalate.

Three peaks were classified by comparing the retention time and UV spectra of 1,4-benzoquinone, parachlorophenol , and 2,5-dichloro-*p*-benzoquinone standard solution. Absorption spectra result was shown in Figure 4(a), Figure 5(a), and Figure 6(a). The compounds were detected at the retention time of 3-5 min (peak 1 in Figure 3 (b)), 9-10 min (peak 2 in Figure 3 (b)), and 10-11 min (peak 3 in Figure 3 (b)) whose absorption spectrum were identical to that of 1,4-benzoquinone (Figure 4), parachlorophenol (Figure 5), and 2,5-dichloro-*p*-benzoquinone (Figure 6), were eluted at the comparable retention time as peak 1, peak 2 and peak 3 (Figure 3(a)), respectively. Moreover, HPLC analysis indicates that the reaction of *p*-DCB yields more than one product. The main product, the peak 3 in Figure 3(b), has ultraviolet spectrum maxima at 272 nm, which is quite similar to that of 2,5-dichloro-*p*-benzoquinone (Figure 6(a)). The TOF-MS spectrum shows a characteristic protonated molecule at m/z =175.9431 corresponding to 2,5-dichloro-*p*-benzoquinone (Figure 7). Other peaks in the solution, such as the peak retention time 1.446 min, 3.073 min, 6.113 min and so on, were not identified because of the limit of the standard materials.

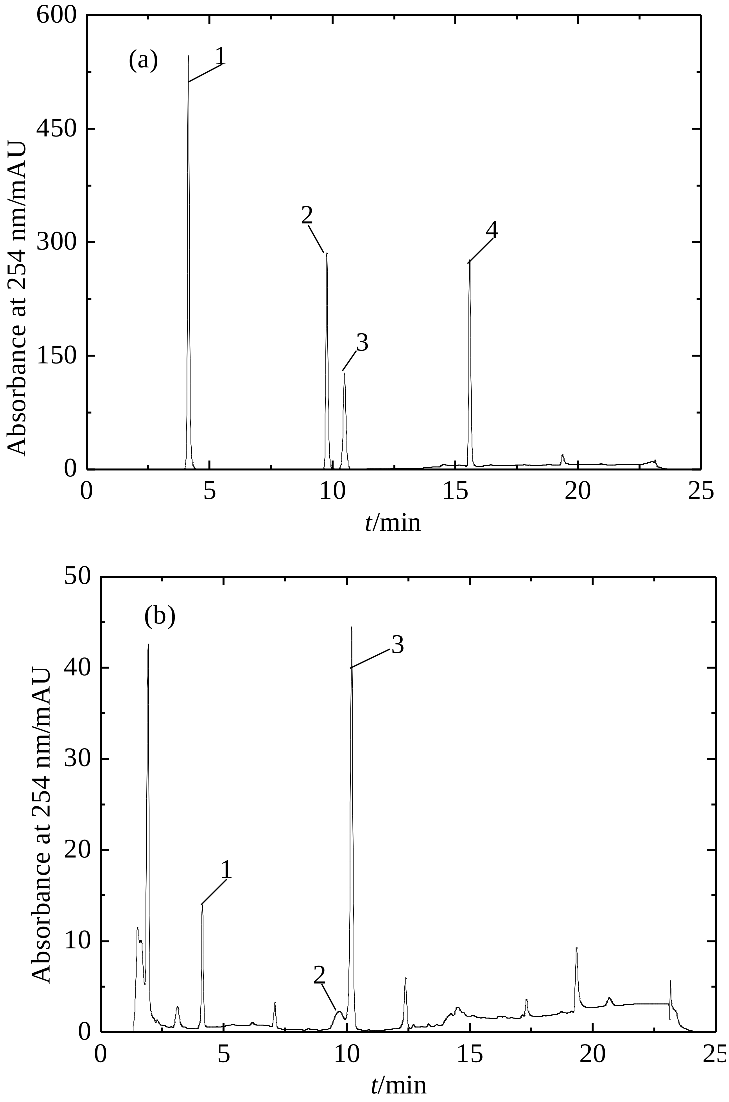


Figure 3. HPLC chromatogram of major chemicals in different combination of solution Note: (a). standard mixture, (b). the intermediate products formed in the electrochemical oxidation degradation of *p*-DCB at 2h; 1. 1,4-benzoquinone, 2. parachlorophenol, 3. 2,5-dichloro-*p*-benzoquinone, 4. 1,4-dichlorobenzene.

The detective (parachlorophenol (D_1), 1,4-benzoquinone (D_3), and 2,5-dichloro-*p*-benzoquinone (D_6))and the tentative states (parahydroquinone (S_2), 2,5-dichlorophenol (S_4), and 2,5-dichlorohydroquinone (S_5)) of the aromatic compounds were displayed both in the table 1. The following study focused on aromatic compounds, which were more toxic than aliphatic hydrocarbon compounds. The degradation mechanism of *p*-DCB was further investigated by CV and chronoamperometric experiments.

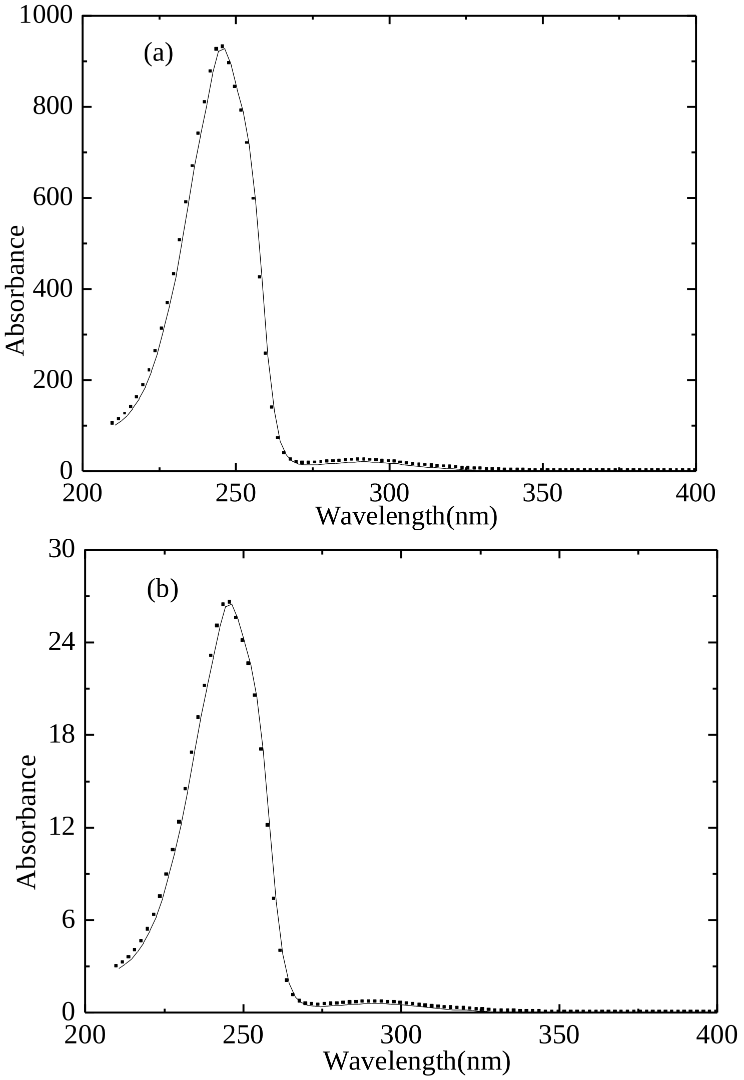


Figure 4. Absorption spectra of 1,4-benzoquinon (Figure 4(a)) compared to those of peak 1 (b) in Figure 3 (Figure 4(b)). The spectra amplitudes were adjusted to the same level at 254 nm.

3.2. Oxidation potential of p-DCB and its intermediates

Considering the oxidation potential of *p*-DCB and its intermediates, the reasons revealed why the compounds could not be detected via organic analysis, and the substances would directly oxidize. If the organic pollutant was verified by direct oxidation on the Pt anode, the anode peak of the compound occurred at less positive potential than the oxygen evolution region. Based on this assumption, a comparison experiment was conducted for elucidating whether any direct oxidation was involved.

Firstly, Figure 8a (1) shows cyclic voltammograms of the Pt disk electrode in blank $NaClO_4$ acetonitrile-water solution. As can be seen, an oxidation peak (1.8 V vs SCE) was observed at less positive potential than oxygen evolution region. According to the literatures [28], the oxidation peak was associated with the Pt oxidation. Moreover, in Figure 8a (2), cyclic voltammograms obtained for oxidation of *p*-DCB. Figure 8a (2) showed that two evident oxidation peaks (1.8, 2.3 V (vs SCE)) could be observed. The former oxidation peak corresponded well with the Pt oxidation peak, while the latter was generally believed as the oxidation peak of *p*-DCB. Herein, this phenomenon was an auxiliary exemplification that *p*-DCB was removed by direct oxidation.

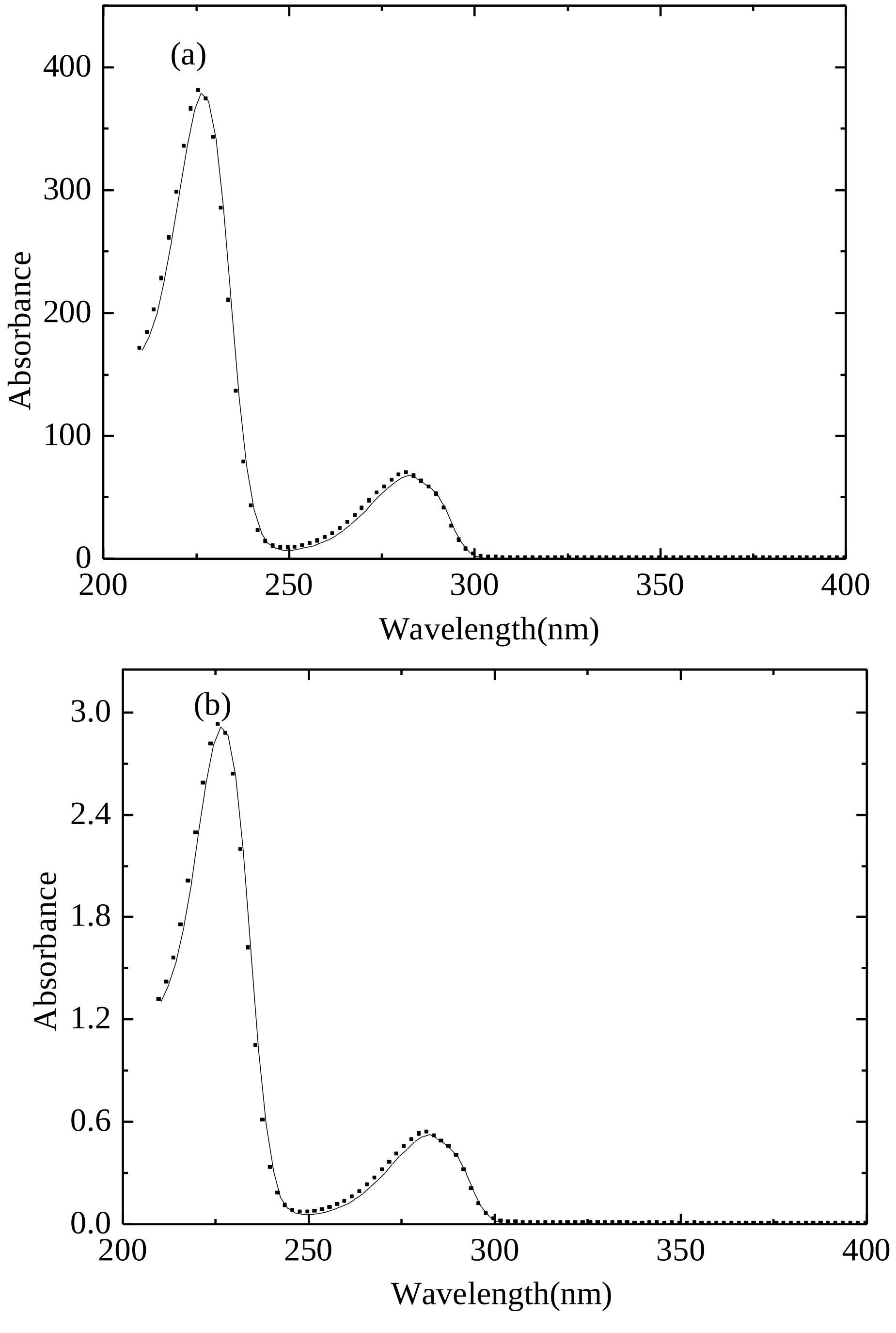


Figure 5. Absorption spectra of parachlorophenol (Figure 5(a)) compared to those of peak 2 (b) in Figure 3 (Figure 5(b)). The spectra amplitudes were adjusted to the same level at 254 nm.

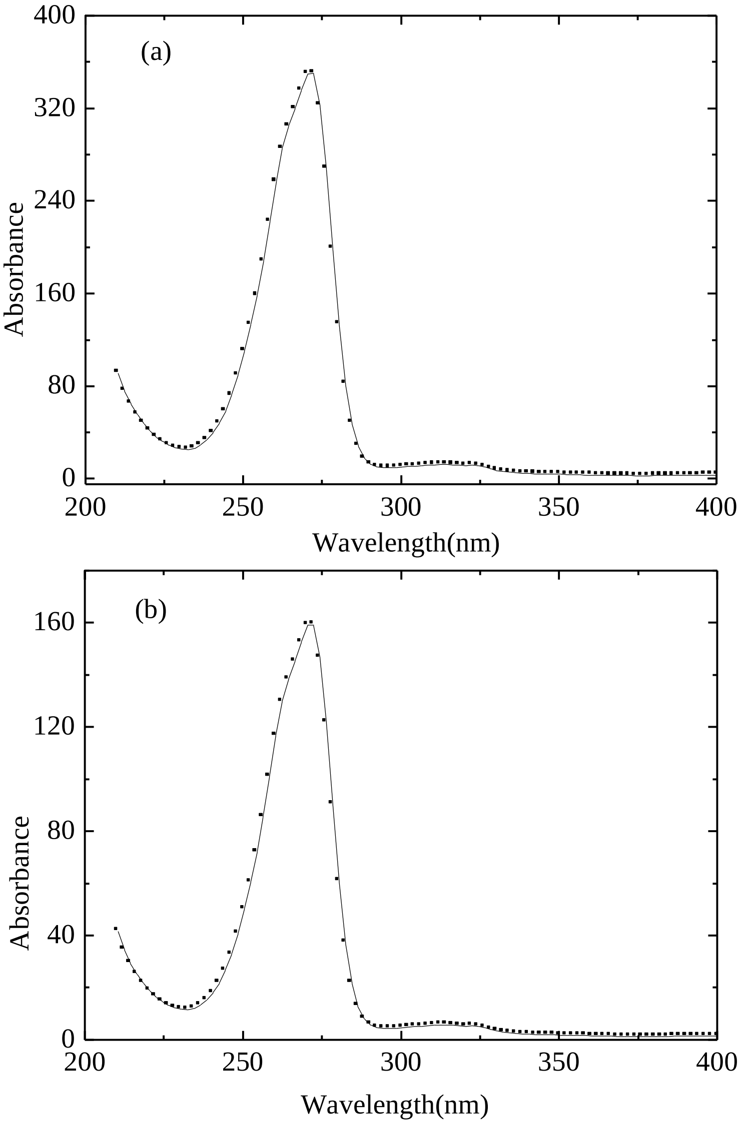


Figure 6. Absorption spectra of 2,5-dichloro-*p*-benzoquinone (Figure 6(a)) compared to those of peak 3 (b) in Figure 3 (Figure 6(b)). The spectra amplitudes were adjusted to the same level at 254 nm.

Secondly, the profiles of the solutions containing D_3, S_2 and D_1 are shown in Figure 8b, respectively. The results shown in Figure 8b (1), an oxidation peak was found at the potential of 1.8 (vs SCE), coinciding with the oxidation potential of Pt. These experimental results confirmed that the direct oxidation of D_3 was not performed in the reaction system mentioned above. However, D_3 could be degraded on the Pt plate electrode [29]. This may be attributed to the indirect oxidation of D_3. In addition, as shown in Figure 8b (2) and Figure 8b (3), the curves of S_2 and D_1 showed two oxidation peaks (0.7, 1.8 V (vs SCE)), and (1.1, 1.9 V (vs SCE)), respectively. The former oxidation peak of S_2 and D_1 were evidently different from the Pt oxidation peak. Therefore, it could be believed that both S_2 and D_1 could degrade by direct oxidation. Comparing Figure 8b (2) with Figure 8b (3), the former oxidation peak of D_1 was more positive than that of S_2, which suggested that the direct oxidation of D_1 was more difficult than for S_2. It was the evidence that S_2 was not detected by HPLC and LC/MS.

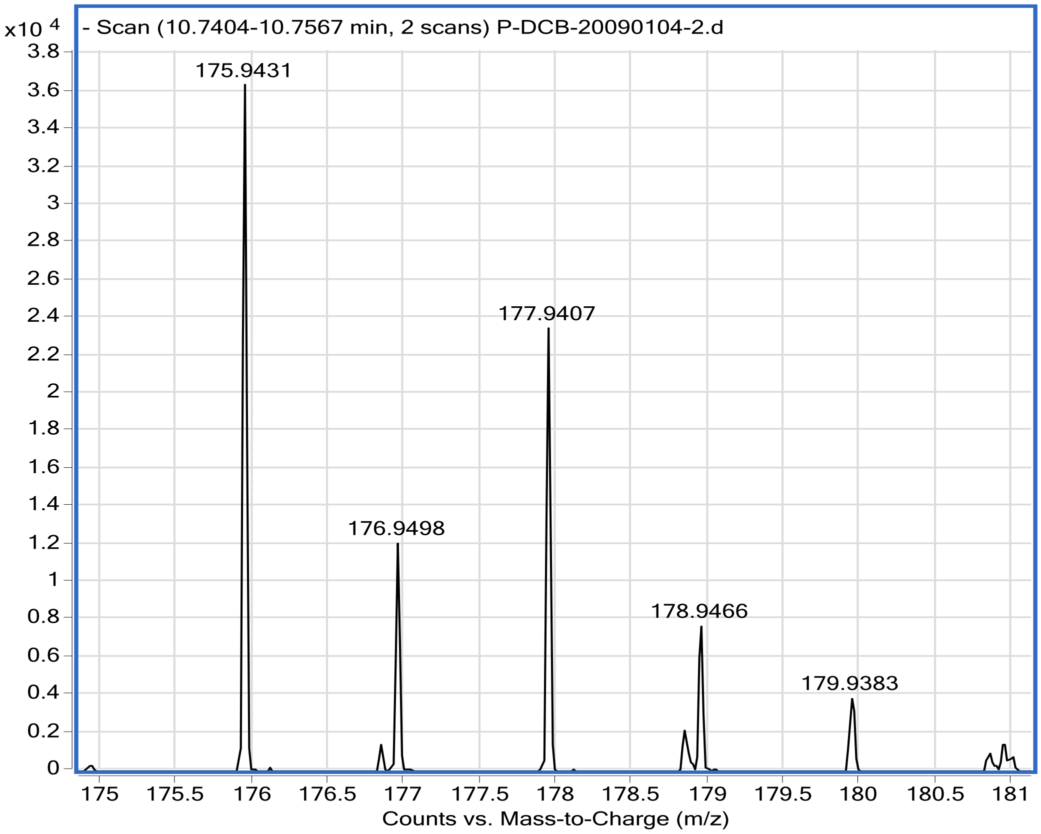


Figure 7. TOF mass spectrum of peak 3 prepared from the reaction in Figure 3(b).

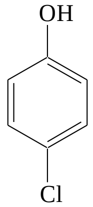
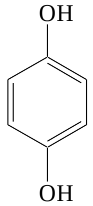
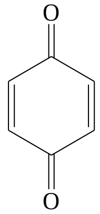
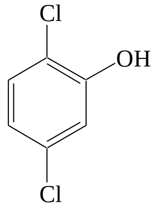
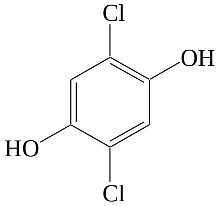
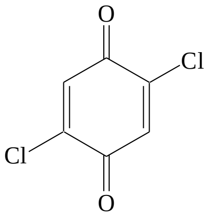
Furthermore, Figure 8c displays cyclic voltammograms of D_6, S_5, and S_4, respectively. In Figure 8c (1), it could be believed that D_6 would not occur by direct oxidation. In addition, from the results in Figure 8c (2) and Figure 8c (3), two oxidation peaks (0.7, 1.8 V (vs SCE)) of S_5 and two oxidation peaks (1.1, 2.2 V (vs SCE)) of S_4 could be observed. The results indicated that both of S_5 and S_4 were directly oxidized. Additionally, comparing Figure 8a (1) with Figure 8c (3), the second oxidation peak of S_4 was more positive than the oxidation peak of Pt. The discrepancy may possibly be attributed to the surface of electropolymerized film of S_4 [30]. Due to strong adsorption of S_4 on the surface of Pt electrode, S_4 was not detected by HPLC and LC/MS. In order to confirm the existence of the polymer film on the surface of Pt electrode, a typical SEM image of the surface, after electrolysis at 2.3 V (vs SCE) in S_4 solution, was shown in Figure 1.

Consequently, the oxidation potential of *p*-DCB and its intermediates could distinguish its different oxidation behaviours (via direct or indirect oxidation) in the static situation, while the electrochemical oxidation mechanism of *p*-DCB could not be explained reasonably in the dynamic processes.

3.3. Assessment of p-DCB and its intermediate products by chronoamperometric measurements

Chronoamperometry techniques enabled the monitoring of rapid dynamic changes in the concentration of substances, and these experimental results suggested that the pollutants were destroyed by either the direct or indirect oxidation process. Moreover, it was possible that the controlled step (diffusion of species to the electrode or electrochemical step) of the electrode process was gradually changed at different reaction stages. It was suggested that if the free radicals (the anode surface through acetonitrile-water discharge) mediated the electrochemical oxidation, the observed current should be independent of the concentration of organic substrate, and if the direct electrochemical oxidation was carried out, the corresponding current should be dependent on the concentration of the organic substrates [19].

Table 1. The aromatic compounds as intermediate products of *p*-DCB

Symbol	Compounds	Structural formula
D_1	parachlorophenol	
S_2	parahydroquinone	
D_3	1,4-benzoquinone	
S_4	2,5-dichlorophenol	
S_5	2,5-dichlorohydroquinone	
D_6	2,5-dichloro-*p*-benzoquinone	

D: intermediates determined by HPLC, IC, LC/MS; S: tentative states

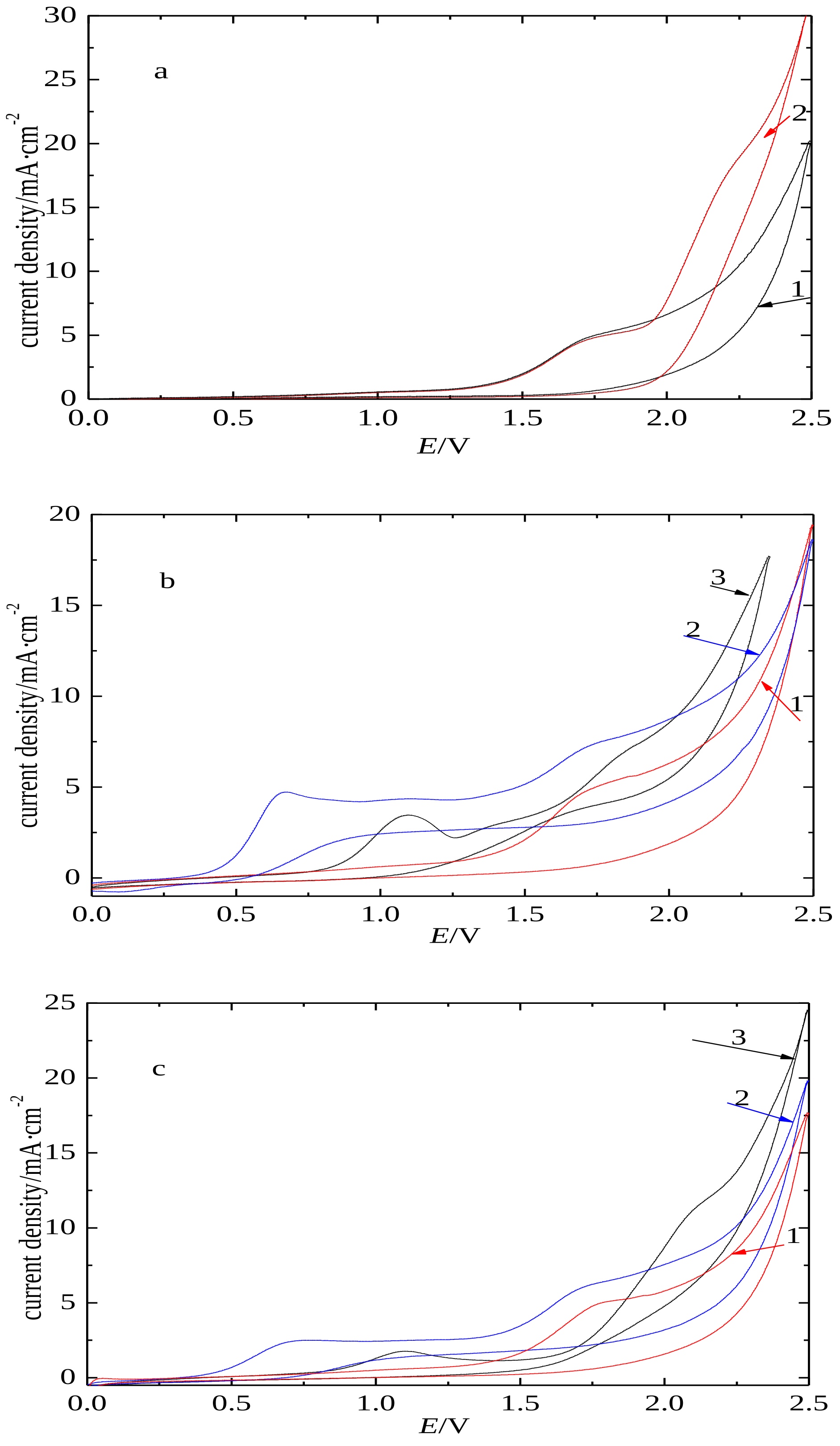


Figure 8. Cyclic voltammograms of the Pt disk electrode in acetonitrile-water solution (v:v, 50:50) containing 0.1 M $NaClO_4$ at a scan rate of 50 mV·s^{-1}. (a(1) (blank solution), a(2) (1.5 g·L^{-1} *p*-DCB), b(1) (1.5 g·L^{-1} 1,4-benzoquinone), b(2) (1.5 g·L^{-1} parahydroquinone), b(3) (1.5 g·L^{-1} parachlorophenol), c(1) (1.5 g·L^{-1} 2,5-dichloro-*p*-benzoquinone), c(2) (1.5 g·L^{-1} 2,5-dichlorohydroquinone), c(3) (1.5 g·L^{-1} 2,5-dichlorophenol).

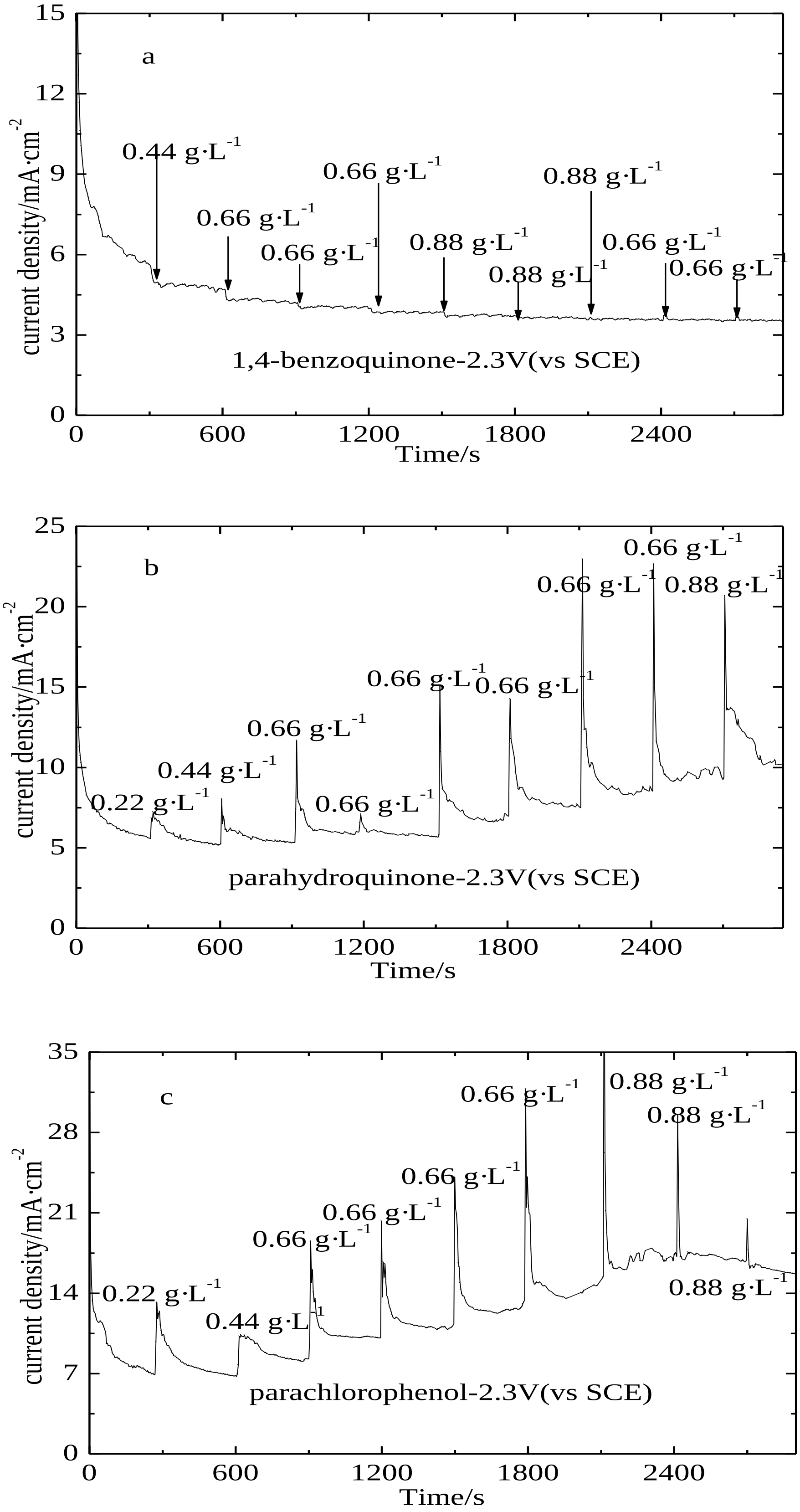


Figure 9. Typical chronoamperometric response of the Pt disk electrode to step-by-step injection of 1,4-benzoquinone (a), parahydroquinone (b), and parachlorophenol (c) in acetonitrile-water solution (v:v, 50:50) containing 0.1 M $NaClO_4$.

On the basis of this assumption, for elucidating whether any direct oxidation took place on Pt disk electrode, a comparison experiment was made by chronoamperometric measurements of current with the different concentration of the intermediates into bulk solution by polarizing the Pt disk electrode (2.3 V vs SCE).

Chronoamporometric experiments were previously investigated at an applied potential of 2.3 V (vs SCE) by some of the authors [17], which was the potential where acetonitrile-water could be discharged and free radicals could be generated. For the first five additions, the current density increased with increasing concentration of *p*-DCB, indicating that oxidation reaction was controlled by diffusion of species to the electrode under low concentrations. Nevertheless, the current density gradually decreased with further additions of *p*-DCB. This fact suggested that the oxidation reaction was controlled by an electrochemical step rather than by diffusion of species to the electrode. Therefore, chronoamperometric measurements showed the possible simultaneous occurrence of different processes such as a direct oxidation at the electrode surface and hydroxyl radical-mediated reaction, a possible adsorption phenomenon, the last one being detectable at higher *p*-DCB concentrations.

In addition, under the same experimental conditions in Figure 9 and Figure 10 at 2.3 V (vs SCE), the different electrochemical reaction steps were known, and the rate-limiting step was identified. As seen in Figure 9a and Figure 10a, the current density decreased with increasing concentration of D_3 and D_6, respectively. It was indicated that the oxidation reaction was controlled by an electrochemical step. Water discharge was inhibited by injection (the step-by-step) of D_3 or D_6 into the solution. The adsorption of D_3 or D_6 molecules also decreased the active sites of the Pt electrode surface in the solution, and therefore, the current for water discharge became lower than the background current at the applied potential. As a consequence, D_3 and D_6 would only occur by indirect oxidation. Comparing the results in Figure 8b (1) with those in Figure 9a, it indicated that the CV experiment of D_3, as well as those chronoamperometric experiments accorded very well with each other at the reaction mechanism. However, Figure 9b and Figure 10b show the current density increased with increasing concentration of S_2 and S_5, respectively. It was suggested that the oxidation reaction was controlled by diffusion of species to the electrode. The chronoamperometric measurements indicated that electrochemical incineration of S_2 and S_5 should be partially attributed to the direct oxidation. Comparing Figure 10a with Figure 10b, the process had not occurred that the current density decreased with increasing concentration of $S_{5.}$ It inferred that the Pt disk electrode displayed good electrocatalytic activity toward the oxidation of S_5. Moreover, the electrode was hardly to be polymerized by electrolysis of S_5. Therefore, S_5 was degraded firstly by direct oxidation. Additionally, as shown in Figure 9c and Figure 10c, for the initial additions, the current density increased with increasing concentration of D_1 or S_4, Nevertheless, the current density gradually decreased with the latter additions of D_1 and S_4, respectively. As a result, D_1 or S_4 at low concentration was degraded mainly by direct oxidation. Otherwise, at high concentrations of D_1 or S_4 could be removed dominantly by indirect oxidation.

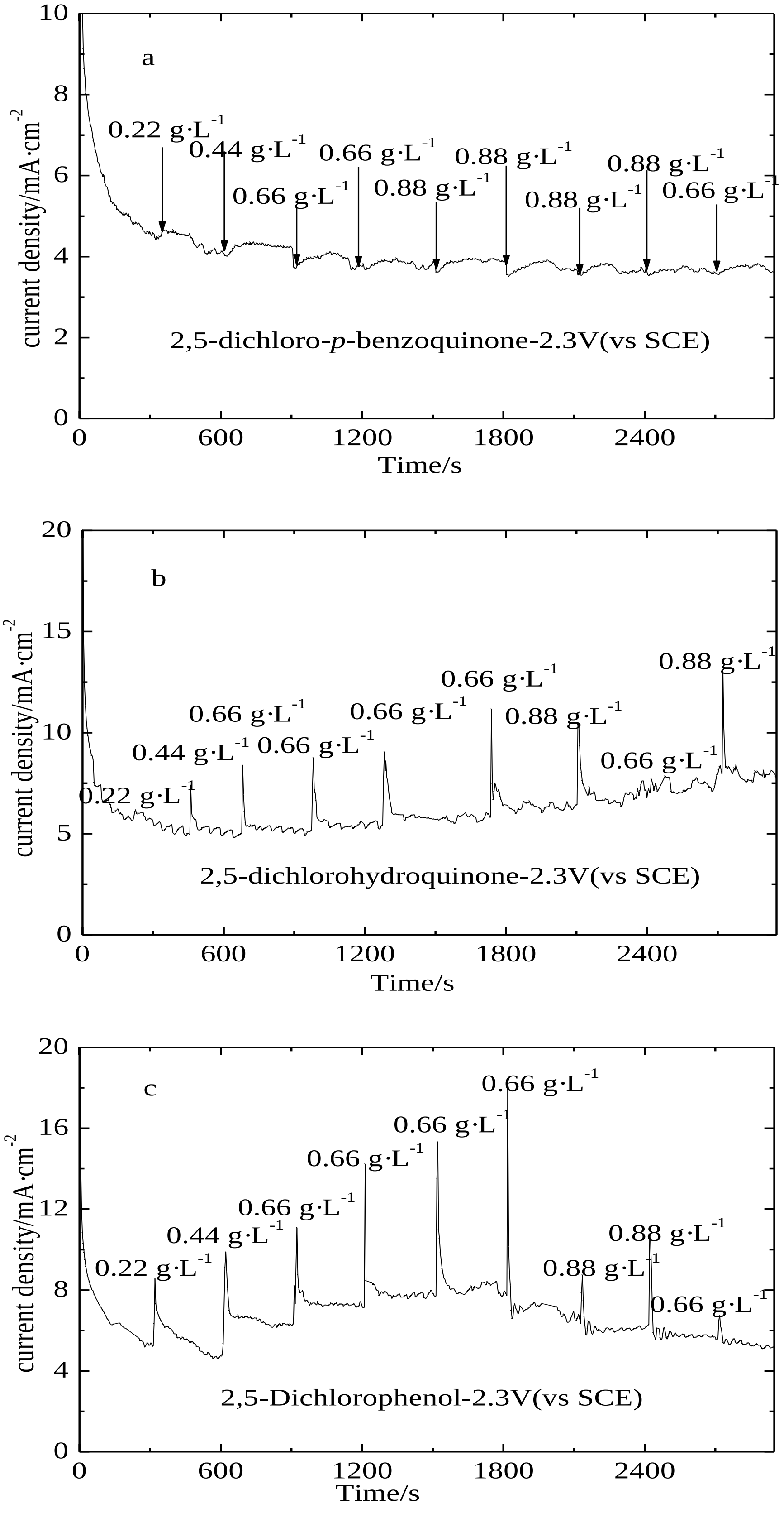


Figure 10. Typical chronoamperometric response of the Pt disk electrode to step-by-step injection of 2,5-dichloro-*p*-benzoquinone (a), 2,5-dichlorohydroquinone (b), and 2,5-dichlorophenol (c) in acetonitrile-water solution (v:v, 50:50) containing 0.1 M $NaClO_4$.

3.4. The mechanism of electrochemical oxidation of p-DCB

The mineralization process of 1,4-dichlorobenzene ($C_6H_4Cl_2$) was accompanied by the release of chloride ions to the medium and could be expressed as follows:

$$12H_2O + C_6H_4Cl_2 \rightarrow 28H^+ + 26e + 2Cl^- + 6CO_2.$$

The reaction indicated the consumption of 26 F for the overall destruction of 1 mol of 1,4-dichlorobenzene.

Based on the above findings, a possible electrochemical oxidation mechanism of *p*-DCB was illustrated by Figure 11. From the results in Figure 11, the process of oxidation in *p*-DCB had the following steps [14, 28]:

$Pt + H_2O \rightarrow PtO_x + 2H^+ + 2e$ (1)
$PtO_x + p\text{-DCB} \rightarrow PtO_x \cdot p\text{-DCB}$ (2)
$PtO_x \cdot p\text{-DCB} - Ze^- \rightarrow PtO_x \cdot S_4 + PtO_x$ (3)
$PtO_x \cdot p\text{-DCB} + PtO_{x+1} \rightarrow PtO_x \cdot S_4 + PtO_x$ (4)
$PtO_x \cdot p\text{-DCB} + PtO_x(\bullet OH) \rightarrow PtO_x \cdot S_4 + PtO_x$ (5)
$PtO_x \cdot S_4 - Ze^- \rightarrow PtO_x \cdot S_5 + PtO_x$ (6)
$PtO_x \cdot S_4 + PtO_{x+1} \rightarrow PtO_x \cdot S_5 + PtO_x$ (7)
$PtO_x \cdot S_4 + PtO_x(\bullet OH) \rightarrow PtO_x \cdot S_5 + PtO_x$ (8)
$PtO_x \cdot S_5 - Ze^- \rightarrow PtO_x \cdot D_6 + PtO_x$ (9)
$PtO_x \cdot D_6 \leftrightarrow D_6 + PtO_x$ (10)
$PtO_x \cdot D_6 + PtO_{x+1} \rightarrow PtO_x \cdot \text{organic acids}$ (11)
$PtO_x \cdot D_6 + PtO_x(\bullet OH) \rightarrow PtO_x \cdot \text{organic acids}$ (12)
$PtO_x \cdot p\text{-DCB} - Ze^- \rightarrow PtO_x \cdot D_1 + PtO_x$ (13)
$PtO_x \cdot p\text{-DCB} + PtO_{x+1} \rightarrow PtO_x \cdot D_1 + PtO_x$ (14)
$PtO_x \cdot p\text{-DCB} + PtO_x(\bullet OH) \rightarrow PtO_x \cdot D_1 + PtO_x$ (15)
$PtO_x \cdot D_1 \leftrightarrow D_1 + PtO_x$ (16)
$PtO_x \cdot D_1 - Ze^- \rightarrow PtO_x \cdot S_2 + PtO_x$ (17)
$PtO_x \cdot D_1 + PtO_{x+1} \rightarrow PtO_x \cdot S_2 + PtO_x$ (18)
$PtO_x \cdot D_1 + PtO_x(\bullet OH) \rightarrow PtO_x \cdot S_2 + PtO_x$ (19)
$PtO_x \cdot S_2 - Ze^- \rightarrow PtO_x \cdot D_3 + PtO_x$ (20)
$PtO_x \cdot D_3 \leftrightarrow D_3 + PtO_x$ (21)
$PtO_x \cdot D_3 + PtO_{x+1} \rightarrow PtO_x \cdot \text{organic acids}$ (22)
$PtO_x \cdot D_3 + PtO_x(\bullet OH) \rightarrow PtO_x \cdot \text{organic acids}$ (23)
$PtO_x \cdot \text{organic acids} \leftrightarrow \text{organic acids} + PtO_x$ (24)
$PtO_x(\bullet OH) + PtO_x \cdot \text{organic acids} \rightarrow PtO_x + CO_2 + ZH^+ + Ze^-$ (25)

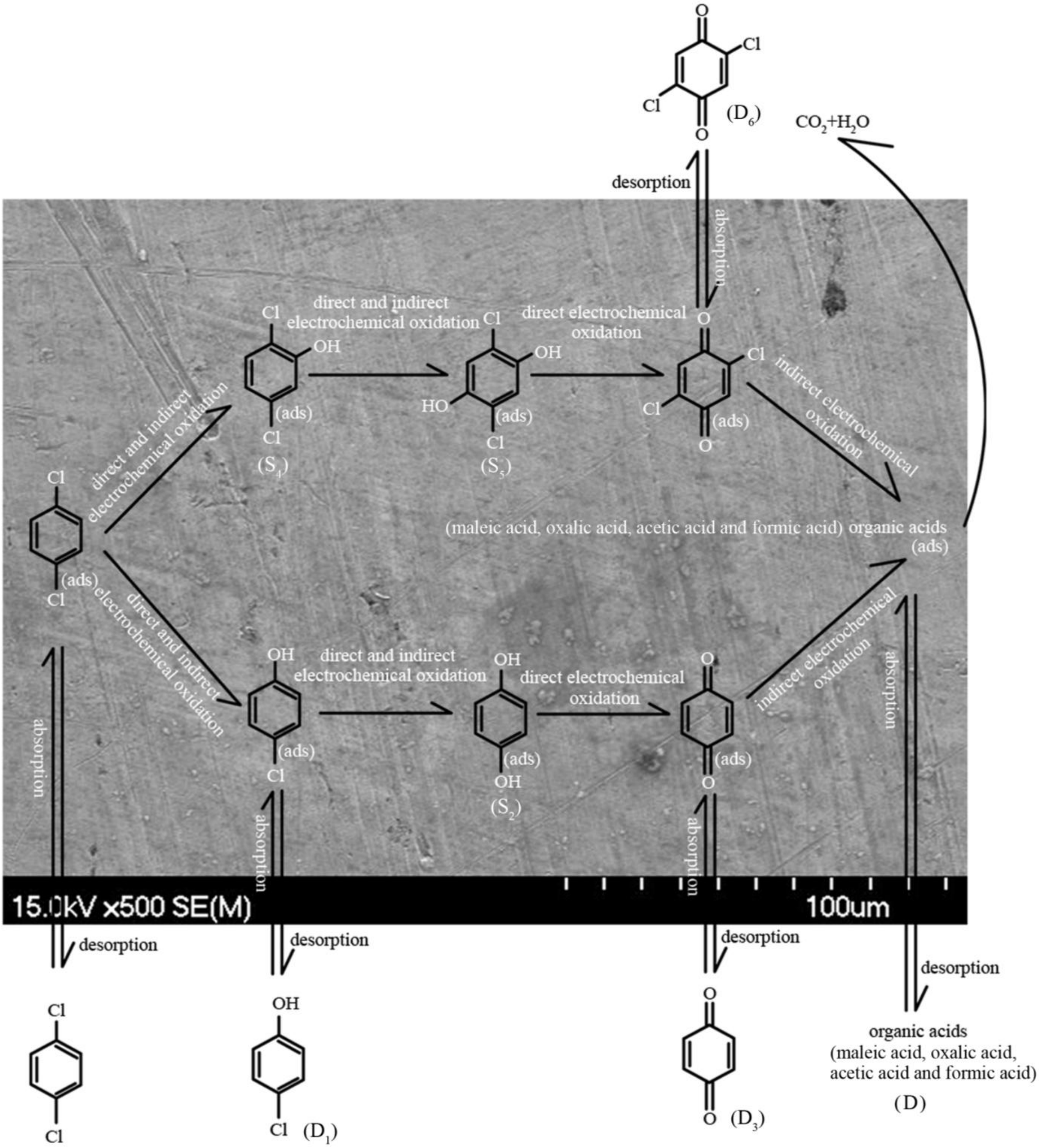


Figure 11. The probable mechanism of electrochemical oxidation of aromatic compounds as intermediate products in acetonitrile-water solution (v:v, 50:50) containing 0.1 M $NaClO_4$.

On one hand, *p*-DCB was controlled by diffusion transfer from the bulk solution to the electrode surface, and the electrode surface of *p*-DCB was soon adsorbed on the electrode being the adsorption of PtO_x ·*p*-DCB. Then, some PtO_x ·*p*-DCB was removed by both direct and indirect oxidation, and came into being the adsorption of $PtO_x \cdot S_4$. And then, it was indicated that both direct and indirect oxidation were responsible for the degradation of $PtO_x\cdot S_4$ forming the adsorption of $PtO_x\cdot S_5$. Electrochemical destruction of $PtO_x\cdot S_5$ could be attempted mainly by direct oxidation being the adsorption of $PtO_x\cdot D_6$, which was degraded by indirect oxidation forming small organic acids. Moreover, part of $PtO_x\cdot D_6$ was desorbed from the electrode surface to the bulk solution.

On the other hand, the results could have represented a combination of direct and indirect oxidation of part of $PtO_x\cdot$*p*-DCB, and came into being the adsorption of $PtO_x\cdot D_1$. Then, Some of $PtO_x\cdot D_1$ was desorbed from the electrode surface to the bulk solution. The degradation of $PtO_x\cdot D_1$ was performed by direct and indirect oxidation being the adsorption of $PtO_x\cdot S_2$, and then $PtO_x\cdot S_2$ was dominantly removed by direct oxidation forming the adsorption of $PtO_x\cdot D_3$. Additionally, $PtO_x\cdot D_3$ was degraded by indirect oxidation. Some of $PtO_x\cdot D_3$ was desorbed from the electrode surface to the bulk solution. Finally, the final substances were water and carbon dioxide, which had been verified by limewater.

4. CONCLUSIONS

We studied the degradation mechanism of *p*-DCB on Pt electrodes in acetonitrile-water solution by the organic analysis combined with electrochemical measurements, and found it to be an effective new methodology for investigating the mechanism of CBs. The methodology allowed the intermediates, the oxidation potential of the intermediates and the mechanism variation with the condition of dynamic changes in the concentration to be determined. Our experiments showed that both direct and indirect electrochemical oxidation processes were involved in the degradation of *p*-DCB. The intermediates such as 1,4-benzoquinone and 2,5-dichloro-*p*-benzoquinone followed the indirect oxidation mechanism, parahydroquinone and 2,5-dichlorohydroquinone were degraded mainly by direct oxidation, and parachlorophenol and 2,5-dichlorophenol were removed by direct and indirect oxidation. An in-depth study was required for the application of these methods in the degradation mechanism of other organic species utilizing electrochemical oxidation.

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