Mechanism of Enhanced Electrochemical Oxidation of 2,4-dichlorophenoxyacetic Acid with in situ Microwave Activated Boron-doped Diamond and Platinum Anodes

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Remarkable enhancement in degradation effect is achieved at in situ activated boron-doped diamond (BDD) and Pt anodes with different extent through electrochemical oxidation (EC) of 2,4-dichlorophenoxyacetic acid (2,4-D) with microwave (MW) radiation in a flow system. Results show that when EC is activated with MW radiation, the complete mineralization time of 2,4-D at the BDD is reduced quickly from 10 to 4 h while Chemical oxygen demand (COD) removal at Pt is increased from 37.7 to 58.3% at 10 h; the initial current efficiency is both improved about 1.5 times while the pseudo-first-order rate constant is increased by 153 and 119% at the BDD and Pt, respectively. To gain insight into the higher efficiency in microwave activated EC, the mechanism has therefore been systematically evaluated from the essence of electrochemical reaction and the accumulated hydroxyl radical concentration. 2,4-Dichlorophenol, catechol, benquinone, and maleic and oxalic acids are the main intermediates on the Pt anode measured by high performance liquid chromatography (HPLC), while the intermediates on the BDD electrode include 2,4-dichlorophenol, hydroquinone, and maleic and oxalic acids. The reaction pathway with microwave radiation is the same as that in a conventional electrochemical oxidation on both electrodes. While less and lower aromatic intermediates produce at the BDD with MW, which suggests the higher ring-open ratio and the faster oxidation of carboxylic acids. With microwave radiation, the ring-open ratio at the BDD is increased to 98.8% from 85.6%; the value at Pt is increased to 67.3% from 35.9%. So microwave radiation can activate the electrochemical oxidation, which leads to the higher efficiency. This promotion is mainly due to the higher accumulated hydroxyl radical concentration and the effects by microwave radiation. All the results prove that the BDD electrode presents much better mineralization performance with MW. To the best of our knowledge, it is the first time the systematic analysis of the mechanism of microwave activated EC has been reported.

1. Introduction

In recent years the electrochemical method (EC) has been applied in the wastewater treatment, which is environmentally compatible with the cleanest oxidant, electron, and without secondary pollution. The technology presents some significant advantages, such as versatility and higher energy efficiency, without production of sludge, is easy to automate, and attracts more attention for wastewater treatment.[1,2] However, in the treatment of pollutants with electrochemical oxidation, the current efficiency is usually higher at the initial reaction stage and then becomes lower later, even to a complete halt of the process.[3] The reason is that pollutants and their intermediates are often adsorbed on the electrode surface during the oxidation and reduce the active sites on the electrode surface, resulting in partial or complete poisoning of electrode and a decrease in current efficiency. For an economical electrochemical oxidation, persistently higher oxidation efficiency is required. Recently, traditional heating,[4,5] microwave,[6,7] ultrasound,[5,8] laser,[5,9] and some other physical methods[10] are used for activation of the electrode surface reaching a higher oxidation efficiency.

Microwave (MW) radiation has been applied in chemical reactions and the treatment of environmental pollutants because of its thermal[11] and catalytic effects.[12] The application of microwave radiation combined with some other methods has also been explored. For example, the combination of microwave radiation and photocatalysis was effective in increasing the degradation efficiency.[13] The localized superheating at the microelectrode surface by microwave radiation[5,6,14] enhanced the electroanalytical performance of the electrode. In our previous study, it was also shown that microwave radiation can activate electrochemical oxidation; the flow system was adopted to avoid the continuous increase in temperature and pressure induced by microwave irradiation, and this method was preliminarily used to removal of pollutants.[15] In addition, microwave radiation can improve the photoassisted degradation of pollutants, which is because the microwave radiation provides not only the heat source (as the thermal effect) but also a specific effect (the nonthermal effect).[16] The nonthermal effect may be that microwave can enhance the ion mobility and the diffusion of charge carriers to the surface, increasing the formation of $OH^{\bullet}$ radicals and the concentration of electrons at the surface.[17] So the nonthermal effect may be beneficial to the electrochemical oxidation.

Horikoshi[17] et al. has been pointed out microwave radiation has thermal and nonthermal effects in the photoassisted degradation of pollutants. This is the same for the electrochemical oxidation process. The thermal effect causes the solution temperature to increase, leading to improved mass transport. And microwave radiation also can accelerate OH radicals generated on the electrode surface, which can alleviate electrode passivation, as the extra electrochemical effect. All these are favorable to the electrochemical oxidation. So the effects by microwave radiation, and the mechanism of enhancement in

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the microwave activated electrochemical oxidation (MW-EC), are investigated in our work. As is known, in the electrochemical oxidation of pollutants, the passivation of the electrode depends on the initial pollutant and its intermediates, the passivation may be different for different electrodes, and the improvement by the in situ microwave activation for different electrodes is different. The different passivation and activation are closely related to the property of the electrode. The generation of hydroxyl radicals is the important ability of the electrode in the electrochemical oxidation of pollutant. The improvement of hydroxyl radicals may be different for different electrodes by microwave radiation. Thus the mechanism of the enhancement in the MW-EC process is discussed from intermediates, the accumulated hydroxyl radical concentration and the effects of the MW radiation.

In this work, boron-doped diamond (BDD) and Pt electrodes are used for this study. The Pt electrode is a typical electrode. It has many outstanding characteristics, such as high chemical stability, electrocatalytic performance (especially dehalogenation[18,19] for organic oxidation), selective oxidation,[20] ease of control, ease of installation, and access to large areas for applications. However, the Pt electrode is often passivated by pollutants and their intermediates.[1] The BDD is an excellent material with special electrochemical properties, such as the inert surface with low adsorption properties, remarkable corrosion resistance, and an extremely wide potential window in aqueous medium.[21] It is superior in oxidation of pollutants, in which the pollutants are mineralized by $OH^{\bullet}$ produced on the electrode surface and removed.[22,23] So the investigation on the mechanism of enhancement on the different BDD and Pt electrodes in the MW-EC process may be significant for the pollutants treatment.

2,4-Dichlorophenoxyacetic acid (2,4-D) is our target pollutant to study the mechanism of the enhancement in the MW-EC process. 2,4-D belongs to chlorophenoxyacetic herbicides and is used worldwide for weed control on cereal crops, grassland, and sand lawns. Their chloroderivative products have more toxicity toward humans and animals. They generate waste products and contaminate waters. Thus, there is a great interest in developing efficient oxidation methods to remove chlorophenoxyacetic herbicides. Many electrochemical oxidation methods have also been applied to mineralize 2,4-D in aqueous solutions.[24–26] However, 2,4-D is an aromatic acid herbicide and its intermediates include phenolic and quinonic compounds, which cause the passivation of the electrode leading to the decrease of degradation efficiency.[27] The microwave activation may be helpful to reduce the passivation and activate the electrode reaching higher efficiency.

Our present work focuses on investigating a new method of microwave in situ activated electrochemical oxidation of pollutant, which can increase the oxidation current efficiency. The different enhancements in electrochemical oxidation of 2,4-D with MW radiation at BDD and Pt electrodes are compared in detail from oxidation current efficiency and kinetic parameter. The mechanism of microwave in situ activated electrochemical oxidation is also discussed systematically from the intermediates, the accumulated hydroxyl radical concentration in the solution, and the effects of microwave radiation. Moreover, to our best knowledge, the systemic work has not been reported. This detailed study will be helpful to develop the microwave activation electrochemical oxidation in the pollutants treatment.

2. Experimental Section

Chemical Reagents. 2,4-D was reagent grade from Sigma. 2,4-dichlorophenol, hydroquine, benquinone, oxalic acid, fumaric acid, dimethyl sulfoxide, 2,4-dinitrophenylhydrazine, organic solvents, and other chemicals used were analytical grade. All solutions were prepared with deionized water.

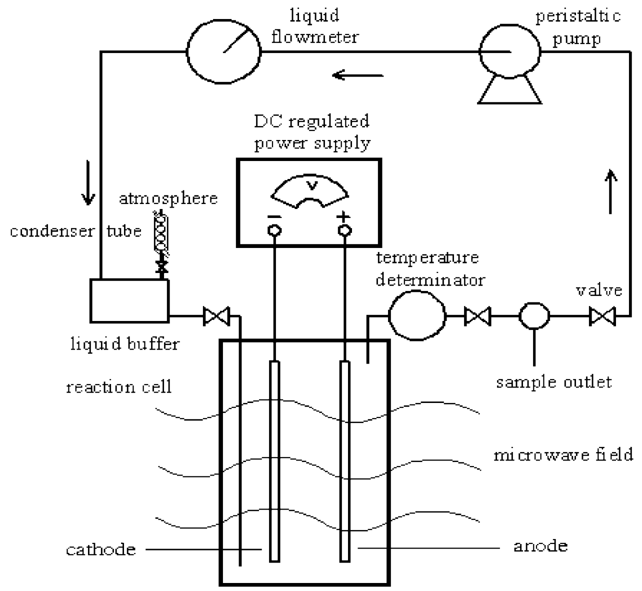


Figure 1. Schematic diagram of experimental setup.

Electrochemical Degradation. A modified domestic microwave oven (Panasonic NN-GT557M, Panasonic Corporation, Japan) of the experimental setup shown in Figure 1 was used for supplying the microwave energy. Microwave "transparent" Teflon (PTFE) was chosen as the material of the reaction vessel, and a poly column reactor was installed into the microwave oven. 2,4-D solution was added continuously into the flow reactor by a peristaltic pump, and the buffer pool was connected with a condenser tube, which is open to the atmosphere. Moreover, the buffer pool was installed in a constant-temperature bath of 291.15 K; thus the system was carried out at a mild temperature and under atmospheric pressure. High temperature and pressure being caused by microwave radiation were well resolved. The flow rate was 150 mL min^{-1}, and the reactor contained 90 mL of 2,4-D solution.

Due to the microwave output port in the right side of the microwave oven chamber, the opening was placed on the left at the top center. The 32 mm diameter opening serves as the channel for the reaction liquid and electrochemical wire. To prevent leakage of microwaves around the opening, a cutoff waveguide of copper tube is installed at the opening. To further check the leakage of microwaves, a device choke is installed in the copper tube. An RCQ-1A microwave leakage determinator was used to measure the microwave power at 5 cm above the surface of the microwave oven before each experiment. The result was less than 1 mW cm^{-2}, which meets the international standards. The frequency of the microwave was 2450 MHz, and the output power was 127.5 W in the experiments. The depth of the tube in the solution depended on the volume of the solution.

The electrolysis was conducted in a cylindrical single-compartment cell containing 90 mL solution. The anode was a 5.5 cm^2 BDD thin film deposited on a conductive Si sheet purchased from Switzerland. Pt also worked as an anode. A titanium bar with the same surface area was used as the cathode, and the gap between the electrodes was 2 cm. The solution was electrolyzed at a constant current (I) of 55 mA. 2,4-D solution of 100 mg L^{-1} was degraded in an aqueous medium containing 0.05 M Na_2SO_4 as supporting electrolyte. MW-EC degradation was carried out at the frequency of 2450 kHz with the power of 127.5 W, and other conditions were the same as those in the EC process.

The instantaneous current efficiency (ICE) of 2,4-D on the electrode can be calculated as eq 1,[28]

$$\mathrm{ICE} = \frac{FV}{8000I}\frac{\mathrm{d(COD)}}{\mathrm{d}t} \tag{1}$$

in which ICE was the instantaneous current efficiency (%), d(COD) was the COD variable quantity in dt time (mg L^{-1}), t was the electrolysis time (s), I was the current (A), V was the electrolyte volume (L), and F was the Faraday constant (C mol^{-1}). The standard colorimetric (titrimetric) method with closed reflux was used to determine the COD.

The aromatic intermediate ratio, which is the percentage of 2,4-D converted into aromatic intermediates relative to the amount of 2,4-D converted, is defined as[29]

$$\%\ \mathrm{Aromatics} = \frac{\Sigma[\mathrm{Aromatics}]_t}{(C_0 - C_t) \times n} \times 100 \tag{2}$$

where $\Sigma[\mathrm{Aromatics}]_t$ is the total concentration of aromatic intermediates (2,4-dichlorophenol, hydroquinone, catechol, and benquinone), in mM, C_0 and C_t are 2,4-D concentration at time 0 and t (in mM), and n represents the mole number of 2,4-D converted into aromatic intermediates. So if the % Aromatics is the intermediates without the ring-open ratio, then the ring-open ration is defined as

$$\%\ \mathrm{Ring-open} = 1 - \%\ \mathrm{Aromatics} \tag{3}$$

Analytical Procedure. The hydroxyl radicals were determined according to literature,[30] in which formaldehyde was generated quantitatively by the reaction between hydroxyl radicals and dimethyl sulfoxide (DMSO), and then reacted with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (HCHO−DNPH) and analyzed by HPLC (Agilent HP 1100, Agilent). An Agilent Zorbax Eclipse XDB-C18 column (150 × 4.6 mm, particle size 5 μm) was used at room temperature and with a selected UV detector at $\lambda = 355$ nm. To perform the isocratic elution at a flow rate of 1.0 mL min^{-1}, a mixture of methanol and water (60:40, v/v) was used as the mobile phase.

Evolution of 2,4-D and its aromatic products were measured by HPLC. Chromatographic separations were performed on an analytical Agilent Zorbax Eclipse XDB phenyl column (4.6 × 150 mm, 5 μm) at room temperature and with the UV detector at $\lambda = 283$ nm. Generated carboxylic acids were detected and quantified on an Ultimat TMAQ-C18 column (4.6 × 100 mm, 5 μm) at room temperature and with a selected UV detector at $\lambda = 210$ nm. For these analyses, a 50:50 (v/v) acetonitrile/0.2% acetic acid mixture for the phenyl column and a buffer (pH = 2.3) of 1:2 (v/v) 50 mmol NaH_2PO_4/50 mmol H_3PO_4 for the AQ-C18 column were employed as the mobile phase at the flow rate of 1.0 mL min^{-1}. In both cases, 20 μL aliquots were injected into the HPLC.

The temperature at the electrode surface, $T_{\mathrm{electrode}}$, was determined from voltammetric experiments, which were carried out in a conventional three-electrode cell using CHI 660 electrochemical workstation (CHI Co.). BDD and Pt electrodes were used as the working electrode, with a saturated calomel electrode (SCE) as a reference, and Pt as a counter electrode. The $Fe(CN)_6^{3-/4-}$ redox system in 1 M KCl aqueous exhibited a shift of dE/dT = −1.53 mV/K.[16,31] All potentials in this work were against SCE.

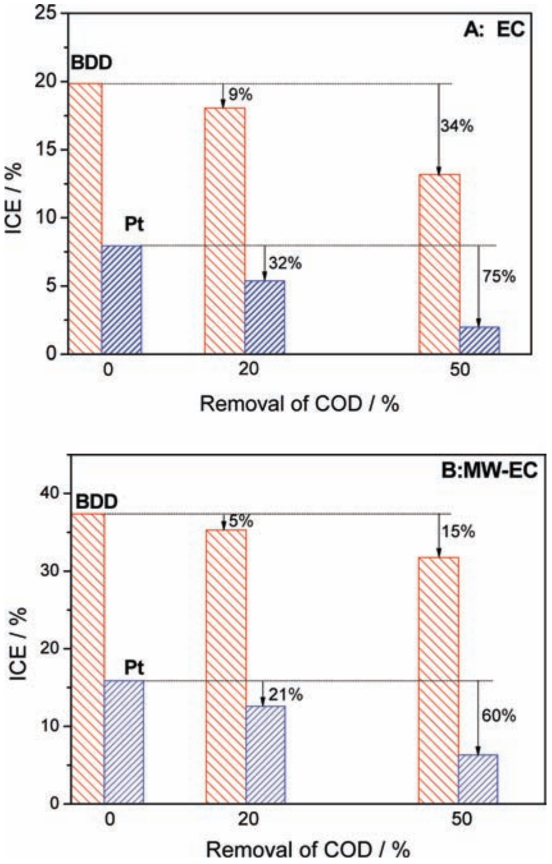


Figure 2. Variation of ICE for removal of COD on BDD and Pt anodes in a 100 mg L^{-1} 2,4-D solution.

The diffusion coefficient (D) of 2,4-D on the electrode surface are determined by the one-step chronocoulometry method in EC and MW-EC processes, respectively. In which the Cottrell formula[32,33] is used

$$Q = nFT + Q_{\mathrm{dl}} + 2nFAC^0_{\mathrm{ox}}D^{1/2}t^{1/2}/\pi^{1/2} \tag{4}$$

where Q is the total amount of charge (C·cm^{-2}), A is the real area of electrode (cm^2), C^0_{ox} is the concentration of component in a solution (mol·cm^{-3}), D is the diffusion coefficient of component in water (cm^{-2} ·s^{-1}), t is time (s), Γ is the reaction amount of component at the electrode surface (mol ·cm^{-2}), Q_{dl} is the number of coulombs required for double-layer charging (C·cm^{-2}), and n is the number of electrons per pollutant molecule transferred in the oxidation reaction on the electrode. The diffusion coefficient and reaction amount of 2,4-D in EC and MW-EC processes were calculated according to the Cottrell formula.

3. Results and Discussion

Microwave activation of BDD and Pt Electrodes. The treatment efficiency of the electrode in each treatment can be explained from its ICE. The evolution of ICE in EC and MW-EC processes is shown in Figure 2. In the EC process, ICE at the Pt electrode is 5.4 and 2.0% when COD removal is 20 and 50%, respectively, decreased by 32 and 75% compared with the initial value of 7.9%. Correspondingly, ICE at the BDD electrode is 18.1 and 13.2%, decreased by 9 and 34%, respectively. In the MW-EC process, when COD removal is 20 and 50%, ICE at Pt is 6.3 and 12.6%, dropped by 21 and 60%, respectively, while the value at the BDD electrode is 31.7 and 35.3%, dropped by 5 and 15%, respectively. So ICE decreases more slowly than in the EC process. That is to say, ICE increases with microwave radiation. When COD removal is 20 and 50%, ICE increases by 134 and 218% at Pt, respectively. The value at the BDD is 96 and 141%, respectively. Due to the high initial ICE, ICE at the BDD is higher than that at Pt in both processes. This indicates that microwave radiation can enhance the current efficiency. However, ICE at Pt is far lower than that at the BDD in both processes. This is contributing to the superior oxidation ability of the BDD. In the EC process, ICE declines with COD removal, the main reason is that the 2,4-D concentration becomes lower with electrolysis time, and oxygen and hydrogen evolution play a major role increasingly. In addition, the active sites on the electrode surface are blocked by initial pollutant and its intermediates leading to the electrode passivation. This can also result in the decrease of ICE. Moreover, ICE decreases on the Pt electrode more quickly than that on the BDD electrode. This indicates that the passivation is more serious on the Pt electrode. While in the MW-EC process, ICE on both electrodes is higher than that in the EC process. The main reason is that microwave radiation can accelerate the mass transport and other effects by microwave radiation, all these factors can activate the electrode, leading to the higher oxidation efficiency. This will be further discussed on the subsequent section.

To understand the passivation of BDD and Pt electrodes and the microwave activation in the electrochemical oxidation, a study on the intermediates was carried out. The intermediates and their concentration change are not identical at both electrodes. However, the intermediates at the same electrode are identical, the difference is the evolution of the intermediates. So the reaction pathway with microwave radiation is the same as that in a conventional electrochemical oxidation on both electrodes. The evolution of aromatic intermediates is shown in Figure 3. In the EC process, 2,4-dichlorophenol, catechol, and benquinone are the intermediates produced at the Pt electrode. The catechol concentration is relatively high while 2,4-dichlorophenol and benquinone concentrations are low. The concentrations of aromatic intermediates increase first and then decrease, but the catechol concentration remains high, 28.33 mg L^{-1} at 10 h. This is attributed to the superior catalytic ability of Pt, which is favorable to dechlorination,[18,19] but poor mineralization ability for pollutant, especially for aromatic compounds. On the BDD electrode, 2,4-dichlorophenol and hydroquinone are the main aromatic intermediates, their concentration also increases first and then decreases, but differently from the Pt electrode, the hydroquinone concentration is reduced quickly, reaching a very low value of 0.41 mg L^{-1} at 10 h. It may be presumed that BDD and Pt electrodes maintain a good reaction state in the initial stage and present good electrochemical properties and efficient oxidation of 2.4-D and its intermediates. In the later stage of the EC process, phenolic compounds are generated and accumulated heavily on the Pt electrode because of its weak mineralization ability, which electropolymerize on the electrode surface and form a polymer film,[1] resulting in the blocking of active sites, the passivation of Pt electrode, and the decrease of catalytic activity. 2,4-D and its intermediates cannot be oxidized completely, and the catechol concentration remains high and drops slowly in the later stage. The BDD electrode is also poisoned by these phenolic compounds, leading to a less active site on the surface. However, the BDD electrode has better mineralization ability because of its superior electrochemical properties, which results in the lower concentration of hydroquinone and a sharp drop at a later time.

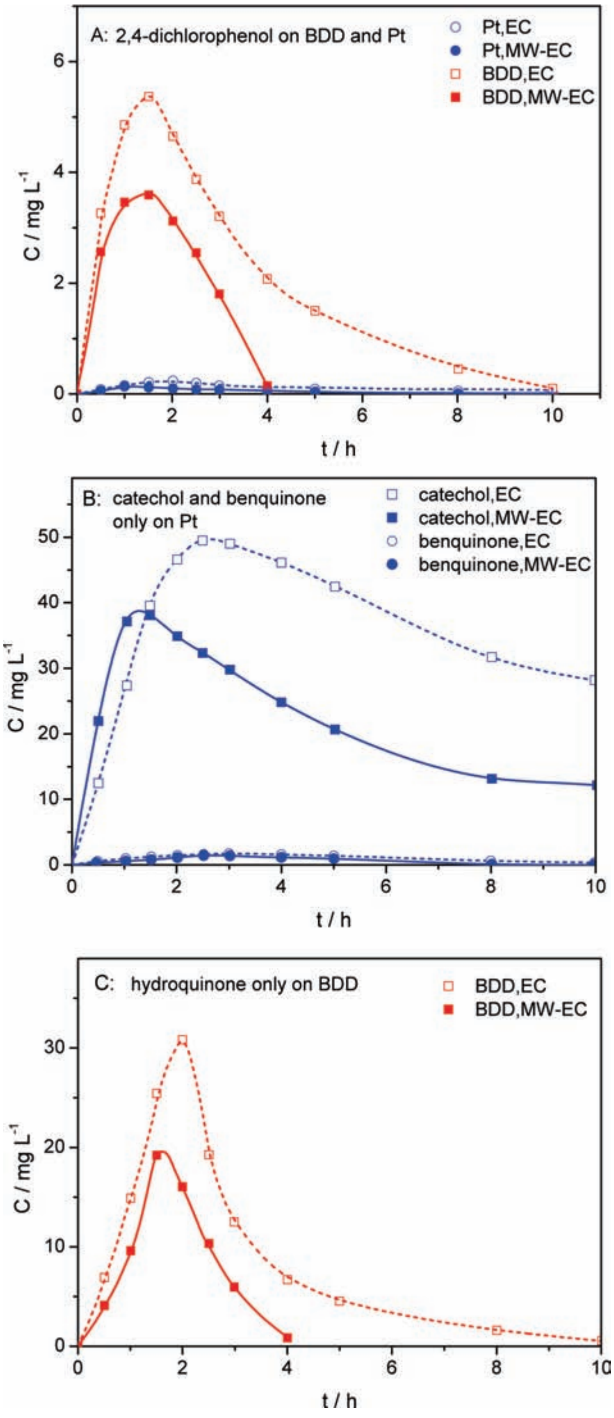


Figure 3. Evolution of aromatic intermediate concentration on Pt and BDD anodes during degradation of a 100 mg L^{-1} 2,4-D solution: (red) BDD electrode; (blue) Pt electrode.

In the MW-EC process, the concentration of aromatic intermediates at both electrodes is lower than that in the EC process. For example, the catechol concentration at Pt is 11.99 mg L^{-1} at 10 h, the hydroquinone concentration at the BDD is 0.75 mg L^{-1} at 4 h, indicating that the BDD has better mineralization ability for the pollutant in the MW-EC process. From the evolution of aromatic intermediates in the MW-EC

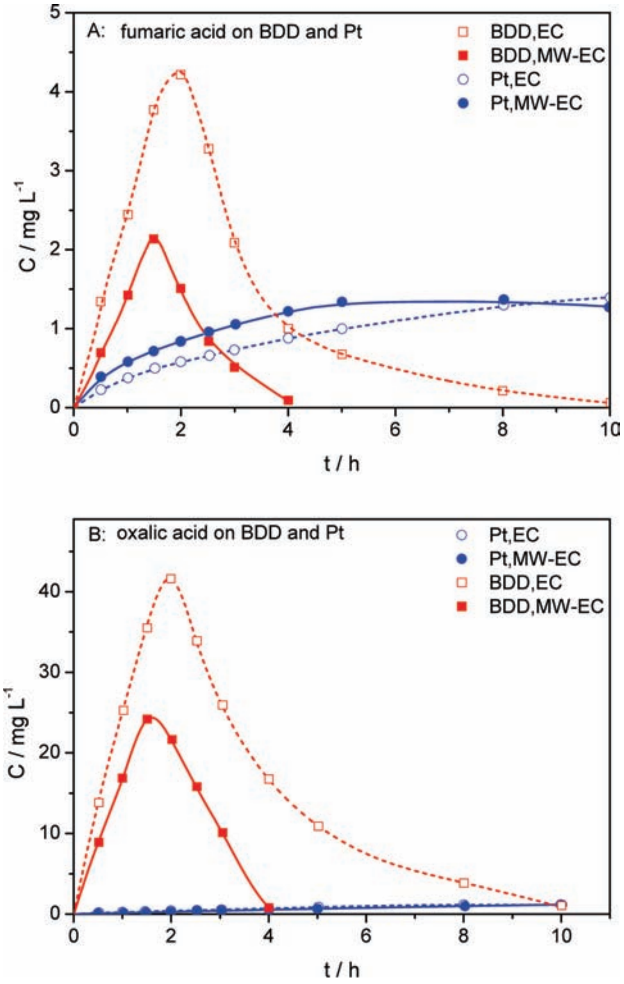


Figure 4. Evolution of carboxylic acid intermediate concentration on Pt and BDD anodes during degradation of a 100 mg L^{-1} 2,4-D solution: (A) fumaric acid; (B) oxalic acid.

process, the variation of their concentration has the same trend with that in the EC process. The diffence is that the aromatics concentration at the BDD drops more quickly, while the value at Pt decrease slightly. This indicates that hydroquinone and catechol are oxidized quickly with microwave radiation, so that the blocking of electrode surface is alleviated, with more active sites on the surface and fewer phenolic compounds. Therefore, microwave radiation enhances the activation of electrode, accelerates the oxidation of phenolic compounds, and improves the electrochemical oxidation efficiency. The catechol concentration being still high at longer times (10 h) shows that the degradation ability of the Pt electrode is enhanced with microwave radiation but fails to reach the complete mineralization.

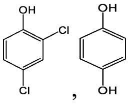
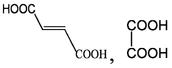
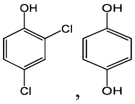
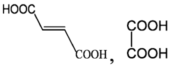
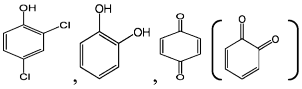
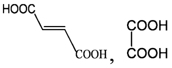
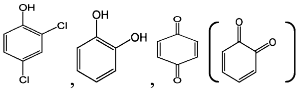
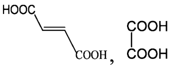
Carboxylic acids include oxalic and fumaric acids. Fumaric acid comes from the destruction of the aromatic intermediates, while oxalic acid is formed from the oxidation of a longer chain carboxylic acid such as fumaric acid.[34,35] The evolution of carboxylic acids is depicted in Figure 4. In the EC process, the concentrations of fumaric and oxalic acids increase very slowly on the Pt electrode because of the passivation by phenolic compounds, which are not oxidized efficiently, leading to the low concentration of carboxylic acid and the slow increase. On the BDD electrode, the two carboxylic acids increase first, leading to higher concentrations of carboxylic acids (ring-open products), which are further oxidized to form CO_2 and H_2O because of their high mineralization ability, and then decrease to a low concentration (0.07 mg L^{-1} for fumaric acid and 1.05 mg L^{-1} for oxalic acid) at 10 h. In the MW-EC process, the concentration of fumaric and oxalic acids also increases slowly, and the value becomes lower than that in the EC process after 9 h. Although, for the BDD electrode, the concentrations of fumaric and oxalic acids have the same trend as that in the EC process, the value is lower and drops more quickly. The value is 0.08 mg L^{-1} for fumaric acid and 0.65 mg L^{-1} for oxalic acid at 4 h. This indicates that both acids are degraded quickly at both electrodes in the MW-EC process, which is attributed to the enhancement on oxidation of electrode by microwave activation. However, the enhancement at Pt is slight, and the intermediates fail to reach complete mineralization in the longer time, while the BDD electrode exhibits higher mineralization ability for intermediates with microwave radiation.

The above analysis shows that the ring-open reactions of aromatic intermediates play a major role during degradation of pollutants. According to eqs 2 and 3, the ring-open ratio (% Ring-open) was further analyzed (Table 1). In the EC process, % Ring-open at the Pt electrode is 35.9% at 4 h. This indicates that in the EC process the reaction is mainly in the aromatic stage, so that the concentration of aromatic intermediates is very high and that of the carboxylic acid is much less. Aromatic intermediates are the major components resulting in the poisoning and passivation of the Pt electrode, and the blocking of the electrode occurs mainly before the ring-opening. At the BDD electrode, % Ring-open is 85.6% at 4 h. The concentration of aromatic and acidic intermediates is very high, so aromatic intermediates and carboxylic acids are the major components resulting in the passivation of the BDD electrode. In the MW-EC process, % Ring-open is 67.3% at the Pt electrode and 98.8% at the BDD electrode. So % Ring-open is also increased at both electrodes. The results show that the electrode is activated by microwave radiation, alleviating the accumulation of intermediates and maintaining more active sites on the electrode. All these lead to the higher electrochemical oxidation efficiency of 2,4-D. For example, the COD removal at 4 h is 46.8% at Pt and 98.2% at the BDD, compared with the values of 26.9 and 46.8% in the EC process, respectively (Table 1). This is same for ICE. ICE at 4 h is 7.5% at Pt and 15.6% at the BDD compared with the values of 4.3 and 10.7% in the EC process, respectively (Table 1). These results show that % Ring-open, COD removal, and ICE are also increased at both electrodes with microwave radiation. However, these values are much higher at the BDD and somewhat higher at Pt in the MW-EC process. This indicates that the BDD electrode has better mineralization ability, and the oxidation ability of the Pt electrode is increased with microwave radiation.

Mechanism of Microwave Activation for BDD and PT Electrodes in the Electrochemical Oxidation Process. Microwave radiation can activate the electrochemical oxidation, leading to the lower concentrations of intermediates. The mechanism of this activation will be discussed as follows.

Microwave is a high frequency electromagnetic wave, which can inevitably cause the thermal effects on the electrochemical oxidation. The temperatures of the solution and the electrode surface will increase under microwave radiation. The temperature was kept constant at 328 K after 8 min due to the application of the flow system, so the reaction occurred at mild temperature and normal pressure. The temperature at the electrode surface, $T_{\mathrm{electrode}}$, was up to 338.95 K on the BDD electrode and 349.15 K on the Pt electrode in the MW-EC process, while it was 293.15 K in the EC process. The instantaneous temperature within a small zone in the neighborhood of the electrode/liquid surface was increased under

TABLE 1: Intermediates, Conversion Rate and Kinetic Parameters of 2,4-D

Reaction	Aromatic intermediates	Acidic intermediates	%Ring-open[a]	Removal of COD[a] / %	k[b] / s^{-1}	ICE[a] / %
BDD, MW-EC			98.8	98.2	2.16×10^{-4}	15.6
BDD, EC			85.6	67.3	8.52×10^{-5}	10.7
Pt, MW-EC			67.3	46.8	3.93×10^{-4}	7.5
Pt, EC			35.9	26.9	1.79×10^{-4}	4.3

[a] These parameters at 4 h. [b] Conversion rate of initial 2,4-D.

microwave radiation. It is favorable to the breaking of the chemical bonds of 2,4-D and its intermediates at the electrode surface, so that the electrochemical oxidation is enhanced.

The temperature of the electrode and the solution can inevitably increase the diffusion coefficient of 2,4-D in the MW-EC process. The diffusion coefficients of 2,4-D in EC and MW-EC processes were calculated according to eq 4. In the MW-EC process, the diffusion coefficients for the BDD and Pt electrodes are 4.80×10^{-4} and 2.82×10^{-6} cm^2 s^{-1}, respectively, while for EC process the values are 5.46×10^{-5} and 9.67×10^{-7}cm^2 s^{-1}, increasing by 7.79 and 2.09 times, respectively. It may be due to the thermal effects on the mass transfer, which is beneficial for 2,4-D and its intermediates to transport to the electrode surface. Similarly in the MW-EC process, the reaction amount on the BDD electrode is 1.69×10^{-9} mol·cm^{-2}, higher than 1.82×10^{-10} mol·cm^{-2} in the EC process, increased by 8.28 times. However, for the Pt electrode, the value is 2.76×10^{-9} mol·cm^{-2} in the MW-EC process, increased by 9.33 times compared with that of 2.67×10^{-10} mol·cm^{-2} in the EC process. With the microwave radiation, the reaction amount is increased, which induced to the amount of contamination participating in reaction increase consumedly, which enhanced the degradation rate.

Another effect by microwave radiation corresponds to the OH$^{\bullet}$ generated on the electrode surface, which is defined as the extra electrochemical effect. As we know, pollutants are degraded mainly by indirect electrochemical oxidation mediated by OH$^{\bullet}$ generated on the electrode surface in the electrochemical process. The accumulated OH$^{\bullet}$ concentration in the solution is shown in Figure 5. It shows that $^{\bullet}$OH radicals are hard to produce with only MW radiation. In both processes the OH$^{\bullet}$ radical concentration increases with electrolysis time, and the values at both electrodes are higher in the MW-EC process than in the EC process at the same time. For example, the hydroxyl radical concentration at the BDD is 22.98 μM at 3 h, which is higher than that of 14.81 μM in the EC process. And the value at Pt is 5.31 μM, while that in the EC process is 3.03 μM. Microwave radiation promotes the generation of OH$^{\bullet}$ radicals, leading to less passivation and more active sites on the electrode, so that the pollutants are oxidized continuously and the electrode fouling is alleviated,[29] which accelerates the 2,4-D oxidation. However, the increment of OH$^{\bullet}$ radicals (ΔC) is different on both electrodes. OH$^{\bullet}$ radicals increase more greatly with electrolysis time on the BDD electrode, while they increase gently on the Pt electrode (see inset of Figure 5). For example, the increment of hydroxyl radical concentration on the BDD is increased to 8.15 μM at 3 h from 2.17 μM at 0.5 h, while the increment on Pt is increased to 2.31 μM at 3 h from 0.62 μM at 0.5 h. In the whole electrolysis process, the accumulated concentration of hydroxyl radicals on the BDD anode with microwave activation is about 1.5−2.1 times that in the conventional electrochemical oxidation, and 1.7−2.1 times that on the Pt anode. So the enhancement of hydroxyl radicals ($C(^{\bullet}\mathrm{OH})_{\mathrm{MW\text{-}EC}}/C(^{\bullet}\mathrm{OH})_{\mathrm{EC}}$) is slightly higher on the Pt anode than that on the BDD anode. However, the enhancement on the Pt electrode increases little in the later reaction stage (after 180 min). Therefore, the mineralization of 2,4-D is not completed on the Pt electrode even for longer times (EC, 16 h; ME-EC, 10 h). In both processes, there are more OH$^{\bullet}$ radicals on the BDD electrode than on the Pt electrode; moreover OH$^{\bullet}$ radicals may exist mainly as free hydroxyl radicals at BDD anodes and react with organic compounds effectively, while the OH$^{\bullet}$ radicals are adsorbed on the other electrodes such as Pt and PbO$_2$.[20] Thus the BDD presents better mineralization performance in the ME-EC and EC processes. Moreover, the performance is much better in the MW-EC process.

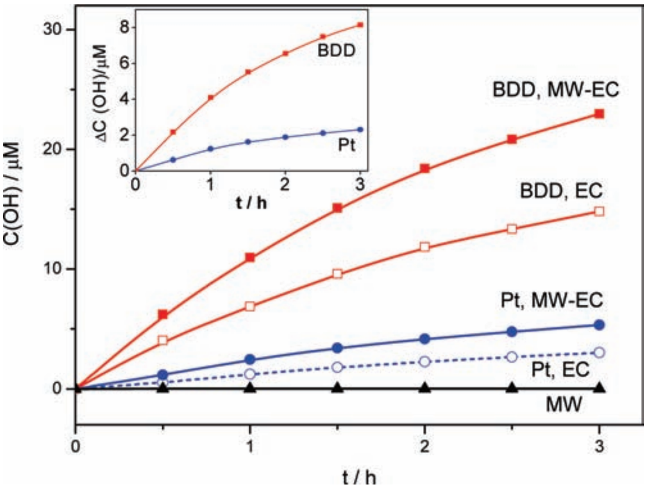


Figure 5. Evolution of hydroxyl radical during the degradation of a 100 mg L^{-1} 2,4-D solution.

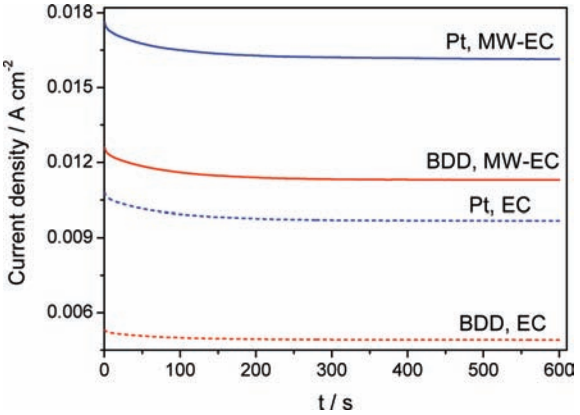


Figure 6. Potentiostatic $I-t$ curves at applied potentials of 4.0 V in 100 mg·L^{-1} 2,4-D solution.

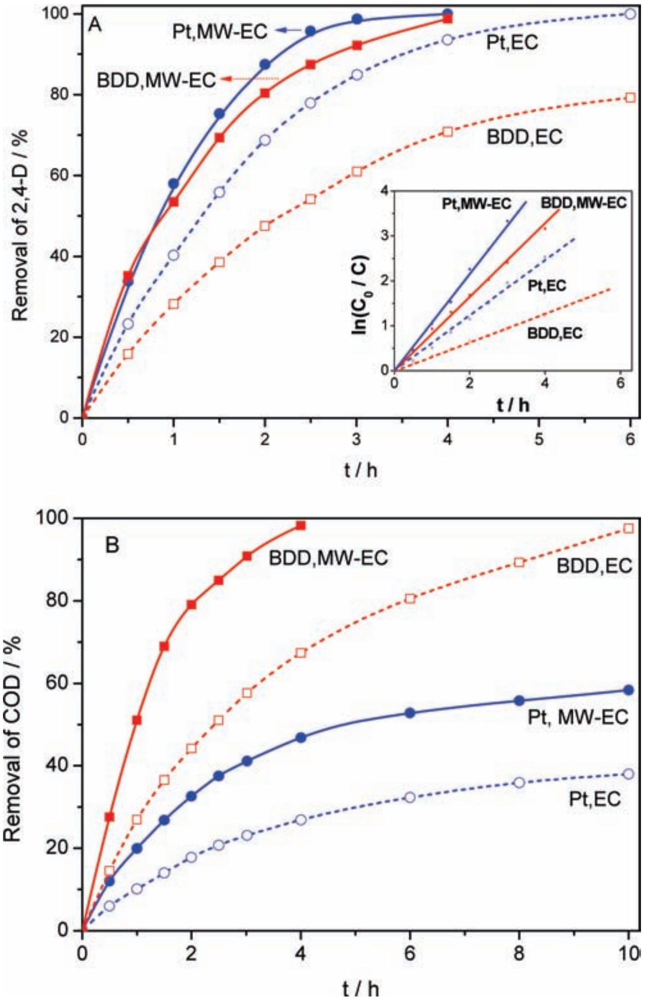


Figure 7. Removal of 2,4-D (A) and COD (B) with electrolysis time for a 100 mg L^{-1} 2,4-D solution. In the inset the linear plots of ln(C_0/C) − t for the treatment of 100 mg L^{-1} 2,4-D solution gives the kinetics of 2,4-D a pseudo-first-order reaction.

The increased hydroxyl radicals with microwave radiation can alleviate the passivation of the electrode, which may accelerate the electrochemical oxidation, also as an extra electrochemical effect. The amperometric $I-t$ curves (Figure 6) are obtained to demonstrate the enhanced electrochemical oxidation by microwave radiation. The potentiostatic $I-t$ curves in the stirred solution are recorded in 100 mg L^{-1} 2,4-D solution at an applied potential of 4.0 V, which is higher than that of the oxygen evolution potential of BDD and Pt electrodes. The steady-state current density is found to be higher in the MW-EC process than in the EC process in both electrodes. The value on the BDD electrode is 1.13×10^{-2} A cm^{-2}, increasing by 1.29 times from 4.91×10^{-3} A cm^{-2} in the EC process, while for the Pt electrode the value is 1.62×10^{-2} A cm^{-2}, increasing by 0.67 times from that of 9.66×10^{-3} A cm^{-2} in the EC process. This may be accounted for by the electrode being activated by microwave radiation, leading to the enhanced electrochemical reaction as the nonthermal effects.

Degradation Effect of 2,4-D on Activated BDD and Pt Electrodes with Microwave Radiation. Microwave can promote OH$^{\bullet}$ radicals generation and alleviate the passivation of electrode, which enhances the removal of 2,4-D. Figure 7A shows that the removal of 2,4-D is higher in the MW-EC process than in the EC process. In the MW-EC process the removal of 2,4-D reaches 98% at 3 h on the Pt electrode, increased by 16% compared to that in the EC process, while the time required to reach the same value on the BDD electrode is 4 h, and the removal of 2,4-D is increased by 39%. The data for 2,4-D concentration decay were further analyzed by kinetic equations with different reaction orders. Good linear plots were obtained when fitted to a pseudo-first-order reaction. The kinetic analysis is depicted in the inset of Figure 7A. The pseudo-first-order rate constants (k) for the MW-EC process are 2.16×10^{-4} and 3.93×10^{-4} s^{-1} on the BDD and Pt electrodes (see Table 1), respectively, increased by 153 and 119%, respectively, compared to those in the EC process. So microwave radiation accelerates the removal of 2,4-D on both electrodes. Moreover, the removal of 2,4-D is higher at the Pt electrode in both processes, due to its superior dehalogenation ability. It does not mean the Pt electrode has a higher mineralization ability because of its lower % Ring-open and fewer OH$^{\bullet}$ radicals generated on the electrode surface. The mineralization of both electrodes is discussed as follows.

The mineralization performance in the MW-EC and EC processes can be illustrated by COD removal of 2,4-D (see Figure 7B). In the MW-EC process, COD removal is 98.2% at 4 h on the BDD electrode, while it takes 10 h in EC process to reaching the same COD removal. This indicates that the BDD electrode has a much higher mineralization ability in the MW-EC process. However, COD removal is far from 98.2% at the Pt electrode in both processes, which means that 2,4-D fails to complete mineralization at the Pt electrode. The COD removal is also increased with microwave radiation. The value is 58.3%, increasing by 55% at 10 h compared with that of 37.7% in the EC process. So microwave radiation can also enhance the mineralization of the two electrodes; moreover, the BDD electrode has much superior mineralization ability, while the enhancement of mineralization ability at the Pt electrode is not high enough to reach the complete mineralization.

4. Conclusions

The mechanism of different enhancement in the electrochemistry of 2,4-D with microwave activation in a flow system is discussed through intermediates, accumulated hydroxyl radical in the solution, and the effects by microwave radiation. 2,4-Dichlorophenol, catechol, benquinone, and maleic and oxalic acids are the main intermediates on the Pt anode measured by HPLC, while the intermediates on the BDD electrode include 2,4-dichlorophenol, hydroquinone, and maleic and oxalic acids. The reaction pathway with microwave radiation is the same as that in a conventional electrochemical oxidation on both electrodes, while fewer and lower aromatic intermediates are produced at the BDD with MW radiation, which lead to the higher ring-open ratio and the faster oxidation of carboxylic acids. The thermal effect of microwave radiation can increase the temperature of the electrode and the solution, and the diffusion coefficient of 2,4-D. The extra electrochemical effect is discussed on the basis of the accumulated concentration of hydroxyl radicals and the steady-state current density. And the enhancement in the accumulated concentration of hydroxyl radicals and the steady-state current density is found to be higher on the BDD anode than on the Pt electrode, which results in the higher degradation effect of 2,4-D on the BDD electrode especial in the MW-EC process.

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References and Notes

(1) Martı'nez-Huitle, C. A.; Ferro, S. *Chem. Soc. Rev.* **2006**, *35*, 1324.
(2) Chen, G. *Sep. Purif. Technol.* **2004**, *38*, 11.
(3) Comninellis, Ch. *Electrochim. Acta* **1994**, *39*, 1857.
(4) Fagan, D. T.; Hu, I. F.; Kuwana, T. *Anal. Chem.* **1985**, *57*, 2759.
(5) Akkermans, R. P.; Roberts, S. L.; Marken, F.; Coles, B. A.; Wilkins, S. J.; Cooper, J. A.; Woodhouse, K. E.; Compton, R. G. *J. Phys. Chem. B* **1999**, *103*, 9987.
(6) Compton, R. G.; Coles, B. A.; Marken, F. *Chem. Commun.* **1998**, *23*, 2595.
(7) Fletcher, P. D. I.; Grice, D. D.; Haswell, S. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1067.
(8) Zhao, G.; Shen, S.; Li, M.; Wu, M.; Cao, T.; Li, T. *Chemosphere* **2008**, *73*, 1407.
(9) Brennan, J. L.; Forster, R. J. *J. Phys. Chem. B* **2003**, *107*, 9344.
(10) Pera-Titus, M.; Garcia-Molina, V.; Banos, M. A.; Gimenez, J.; Esplugas, S. *Appl. Catal., B* **2004**, *47*, 219.
(11) Viirre, R. D.; Evindar, G.; Batey, R. A. *J. Org. Chem.* **2008**, *73*, 3452.
(12) Ai, Z.; Wang, Y.; Xiao, M.; Zhang, L.; Qiu, J. *J. Phys. Chem. C* **2008**, *112*, 9847.
(13) Ju, Y.; Yang, S.; Ding, Y.; Sun, C.; Zhang, A.; Wang, L. *J. Phys. Chem. A.* **2008**, *112*, 11172.
(14) Marken, F.; Sur, U. K.; Coles, B. A.; Compton, R. G. *Electrochem. Acta* **2006**, *51*, 2195.
(15) Gao, J.; Zhao, G.; Shi, W.; Li, D. *Chemosphere* **2009**, *75*, 519.
(16) Sur, U. K.; Marken, F.; Compton, R. G.; Coles, B. A.; New, J. *Chem.* **2004**, *28*, 1544.
(17) Horikoshi, S.; Hidaka, H.; Serpone, N. *J. Photochem. Photobiol. A: Chem.* **2003**, *159*, 289.
(18) Kovalchuk, V. I.; D'Itri, J. L. *Appl. Catal., A* **2004**, *271*, 13.
(19) Orbay, O.; Gao, S.; Barbaris, B.; Rupp, E.; Eduardo Sáez, E.; Arnold, R. G.; Betterton, E. A. *Appl. Catal., B* **2008**, *79*, 43.
(20) Zhu, X. P.; Tong, M. P.; Shi, S. Y.; G Zhao, H. Z.; Ni, J. R. *Environ. Sci. Technol.* **2008**, *42*, 4914.
(21) Gandini, D.; Mahé, E.; Michaud, P. A.; Haenni, W.; Perret, A.; Comninellis, Ch. *J. Appl. Electrochem.* **2000**, *30*, 1345.
(22) Martìnez-Huitle, C. A.; Battisti, A. D.; Ferro, S.; Reyna, S.; Cerro-Loìpez, M.; Quiro, M. A. *Environ. Sci. Technol.* **2008**, *42*, 6929.
(23) Chen, X.; Chen, G.; Gao, F.; Yue, P. L. *Environ. Sci. Technol.* **2003**, *37*, 5021.
(24) Brillas, E.; Boye, B.; Ignasi, S.; Garrido, J. A.; Rosa, M. R.; Arias, C.; Cabot, P.-L.; Comninellis, Ch. *Electrochim. Acta* **2004**, *49*, 4487.
(25) Chu, W.; Kwan, C. Y.; Chan, K. H.; Chong, C. *Chemosphere* **2004**, *57*, 1165.
(26) Wang, Q.; Lemley, A. T. *Environ. Sci. Technol.* **2001**, *35*, 4509.
(27) Gattrell, M.; Kirk, D. W. *J. Electrochem. Soc.* **1993**, *140*, 1534.
(28) Lissens, G.; Pieters, J.; Verhaege, M.; Pinoy, L.; Verstraete, W. *Electrochim. Acta* **2003**, *48*, 1655.
(29) Iniesta, J.; Michaud, P. A.; Panizza, M.; Cerisola, G.; Aldaz, A.; Comninellis, Ch. *Electrochim. Acta* **2001**, *46*, 3573.
(30) Tai, C.; Peng, J.-F.; Liu, J.-F.; Jiang, G.-B.; Zou, H. *Anal. Chim. Acta* **2004**, *527*, 73.
(31) Sur, U. K.; Marken, F.; Rees, N.; Coles, B. A.; Compton, R. G.; Seager, R. *J. Electroanal. Chem.* **2004**, *573*, 175.
(32) Zhang, L.; Jiang, X.; Wang, E.; Dong, S. *Biosens. Bioelectron.* **2005**, *21*, 337.
(33) Zhao, G. H.; Qi, Y.; Tian, Y. *Electroanalysis.* **2006**, *18*, 830.
(34) Brillas, E.; Calpe, J. C.; Casado, J. *Water Res.* **2000**, *34*, 2253.
(35) Boye, B.; Dieng, M. M.; Brillas, E. *Environ. Sci. Technol.* **2002**, *36*, 3030.

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