Electrochemical Incineration of Organic Pollutants on Boron-Doped Diamond Electrode. Evidence for Direct Electrochemical Oxidation Pathway

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The electrochemical incineration of organic pollutants on a boron-doped diamond (BDD) thin film electrode was examined by bulk electrolysis, and the mechanism of oxidation was investigated. A comparative study with other electrodes such as Pt and glassy carbon (GC) electrodes revealed the superiority of the BDD over these electrodes. The extent of degradation of phenol and formate due to direct oxidation and hydroxyl radical-mediated oxidation were quantified by amperometric measurements. The extent of direct oxidation was found to decrease with increasing potentials due to the competing hydroxyl radical-mediated reactions. The extent of direct oxidation for formate was found to be higher than that for phenol, indicating the probability of higher adsorption of formate on the oxygen-terminated diamond surface. Finally, bulk electrolysis of phenol at the BDD resulted in the complete destruction of phenol to CO_2 with a removal efficiency of 96%, indicating the promising use of BDD for electrochemical waste treatment applications.

1. Introduction

The choice of wastewater treatment method depends on the economic possibility of the method as well as on the ease of control, reliability, and treatment efficiency. Because many industrial processes produce toxic pollutants that are not easily biodegradable and require costly physical or physicochemical pretreatment, electrochemical technology (including electro-oxidation, electro-coagulation, electro-flotation, etc.) is becoming a new alternative for the wastewater treatment and is replacing the traditional processes. In particular, the electrochemical oxidation process has been shown to be promising for the removal of organic pollutants from wastewater. In general, organic pollutants can be destroyed electrochemically by conducting a direct anodic oxidation using dimensionally stable electrodes or by an indirect oxidation process, which involves the electrochemical generation of powerful oxidants, such as peroxodisulfuric acid, hydroxyl radical, etc. As the electrons play the role of a clean reagent, electrochemical wastewater treatment technology that needs no additional chemicals is therefore environmentally compatible, versatile, safe, and easy to handle.[1−3]

The practical application of electrochemical oxidation processes to the destruction of organic pollutants in water solution requires a number of essential features. One absolutely essential component is an anode that must be effective in oxidizing. Numerous fundamental investigations and even bench-scale experiments have been done for the anodic treatment of organic pollutants with different anodic materials. However, most anode materials gradually corrode during the use in electrolytic oxidation, especially in harsh chemical environments. Classical electrode materials such as platinum and graphite tend to become deactivated or fouled during electrolytic oxidation of various organic substrates, by the formation of an adsorbed layer of residue on the surface of electrodes or self-oxidation which lowers the effectiveness and shortens the useful life of the anode. Some oxide film electrodes, e.g., RuO_2, PbO_2, and SnO_2,[4−8] exhibiting high oxygen over-voltage, which work efficiently in removing the organic pollutants in comparison to the traditional electrode (e.g., platinum), still lead to discharge of toxic metal materials into the environment. Therefore, an efficient, stable, and environmentally compatible anode material is required for future technology.

On the other hand, ideally, electrochemical oxidation for the organic pollutants is one in which the treated effluent can be directly discharged to the environment, i.e., degradation should produce environmentally acceptable species such as mineral acids and carbon dioxide to achieve zero values of the chemical oxygen demand (COD). The obvious similarities between electrolytic degradation of organic compounds to produce CO_2 and thermal incineration have resulted in reference to this electrolytic approach as "electrochemical incineration"[9] or "electrochemical cold combustion".[10] Such complete degradation depends on the discovery of unique anode materials that possess high oxygen over-voltage or catalytic activity for the requisite anodic O-transfer mechanism.

Recently, synthetic boron-doped diamond (BDD) electrodes fabricated by chemical vapor deposition (CVD) methods, provided electrochemists with an entirely new type of carbon electrode that is especially attractive for electrolysis. The unique electrochemical properties of the BDD electrode that include a wide potential window for water discharge and remarkable stability over prolonged periods of time, even in the most corrosive electrolytes such as acidic fluoride solutions,[11] suggest

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a promising field of application as a dimensionally stable electrode in various electrochemical processes, especially in the treatment of organic waste. So far, some researchers have investigated the electrochemical oxidation of several types of organic pollutants such as phenols and complex agents related to wastewater treatment by the use of the BDD electrode.[12−20] While most researchers devoted their efforts to the examination of stability and COD removal efficiency of these electrodes, a few attempts have been made to give a detailed explanation for the oxidation reaction mechanism of electrochemical incineration and total current efficiency for incineration. Although electrochemical reactions are more or less independent of the condition of wastewater and can proceed as long as a current is supplied to the electrode, the knowledge of the electrochemical behavior of organic pollutants and the electrode reaction mechanism is still important, to develop efficient electrochemical treatment of wastewater.

In the case of "electrochemical incineration" of organic pollutants in water solution, it is usually assumed that the reaction can follow two different pathways. The first one is the direct oxidation at the electrode surface, and the second is indirect electrochemical oxidation mediated by appropriate anodically formed oxidants (including hydroxyl radicals, Cl_2, hypochlorite, peroxide, ozone, Fenton's reagent, peroxodisulfate, etc.). Most of the electrochemical incineration processes on the anode are reported to be mediated and performed via hydroxyl radicals and other active intermediates that are produced on the anode surface by the discharge of water or electrolyte.

For the BDD electrode, it is thought that it could produce and accumulate high amounts of hydroxyl radicals and other active intermediates directly on its surface,[14,17−18] which are promising to incinerate organics to CO_2 due to their high over-voltage to water decomposition. Recently Comninells and co-workers[19] observed the electro-oxidation process of phenolics involving direct electron transfer, in the potential region of water stability (E < 2.3 V vs SHE) on the BDD surface that results in electrode fouling due to the formation of polymeric film on its surface. Therefore, there is one major concern in the field of electrochemical incineration in which BDD is used as the anode, whether oxidation occurs either by direct electron-transfer reaction of organics or by hydroxyl radicals and other activated intermediates, because evidence in support of both mechanisms has been obtained depending on the applied potentials. In fact, it might be desirable as well as necessary to give a fundamental understanding on the electrochemical incineration mechanism at the BDD electrode for its future practical applications.

The present work is a first attempt to investigate the involvement and estimation of extent of direct electron transfer reaction in the electrochemical incineration reaction on the surface of the BDD electrode in the high applied potential region where hydroxyl radical generation is expected at faster rates. A set of experiments was designed to examine whether the oxidation process is consistent with a direct electron transfer pathway or hydroxyl radicals attack in a carefully controlled laboratory condition. Additionally, a comparison of electrolysis efficiencies with Pt and glassy carbon (GC) electrodes is also presented.

2. Experimental Details

2.1. Electrode Materials. Highly doped BDD thin films were prepared by the microwave plasma-assisted CVD system (ASTex, Woburn, MA) on silicon (100) wafers. Prior to deposition, the Si substrates were hand-polished with diamond powder (0.5 μm) for nucleation, following which they were rinsed with 2-propanol. A mixture of acetone and methanol (9: 1, v/v) as the carbon source, and B_2O_3 (Aldrich) dissolved in this solvent was used as the boron source at a B/C molar ratio of 10 000 ppm (i.e., 1 mol %). High-purity (99.99%) hydrogen gas was used as the carrier gas.

The deposition of the film was carried out at a microwave power of 5 kW. A film thickness of 40 μm was achieved after 10 h deposition. The film quality was characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The Raman spectra of this film showed them to be of high quality, as evident from the strong characteristic peak at 1332 cm^{-1}. In addition, a broad peak centered at approximately 1200 cm^{-1} was observed, which is characteristic of highly boron-doped samples.

The glassy carbon plate (GC-20, Tokai Carbon Co., Ltd) electrode was pretreated by polishing with diamond paste (FUJIMI), following by ultrasonication in 2-propanol before the experiment. The Pt plate electrode was also sonicated in 2-propanol.

2.2. Chemicals. Analytical grade phenol and sodium formate were purchased from WAKO-chemicals and TOKYO KASEI. Na_2SO_4 was used as the supporting electrolyte and was used as received. All solutions were made from Milli-Q ultrapure(18 Ω)water.

2.3. Electrochemical Measurements and the Electrolysis System. All of the electrolysis experiments were also performed with a potentiostat (HOKUTO DENKO, HSV-100). Experiments were conducted in batch-mode in an undivided Pyrex glass cylindrical electrolytic cell with a volume of 100 mL and a magnetic stirrer. The anode was a diamond, glassy carbon (GC), or a Pt plate electrode, and the cathode was a Pt plate placed vertically in the center of the cell at a distance of 2 cm from the bottom, the reference is a saturated calomel electrode (SCE). The area of the cathode and anode were the same, 5 cm^2.

2.4. HPLC and COD Analysis. The disappearance of phenolic pollutants during anodic oxidation was measured by a TOSOH MX-8010 HPLC system, UV-200 variable wave-length detector set at 275 nm. Chromatographic separations were performed on an analytical column ODS (a reversed-phase TSK gel, ODS-80Ts; 250 mm long, 4.6 mm i.d.). The mobile phase consisted of acetonitrile and water (60:40 v/v) at a flow rate of 0.5 mL min^{-1}. The column temperature was 40 °C, while the column pressure was 195−200 atm.

Chemical oxygen demand (COD) was determined according to the method described by Jirka and Carter.[21]

3. Results and Discussion

3.1. Evaluation of the Direct Electrochemical Oxidation Pathway on the Surface of the BDD Electrode. As described in the introduction, a major uncertainty for the electrochemical incineration reaction produced on the surface of the BDD anode is whether oxidation occurs by direct electron-transfer reaction on the surface of the anode or by mediation of hydroxyl radicals and other active intermediates produced from water and the electrolyte. According to previous reports,[14,17−18] the BDD electrode, as a "nonactive" electrode, with physisorbed and accumulated OH radicals on the surface of BDD, should predominantly cause complete incineration of organics to carbon dioxide (electrochemical incineration pathway). However, it is well-known that the surface of the BDD electrode consists of sp^3 carbon that causes excellent chemical stability. It is reasonable to expect and has been proved that this type of stable surface might not favor adsorption or accumulation of polar
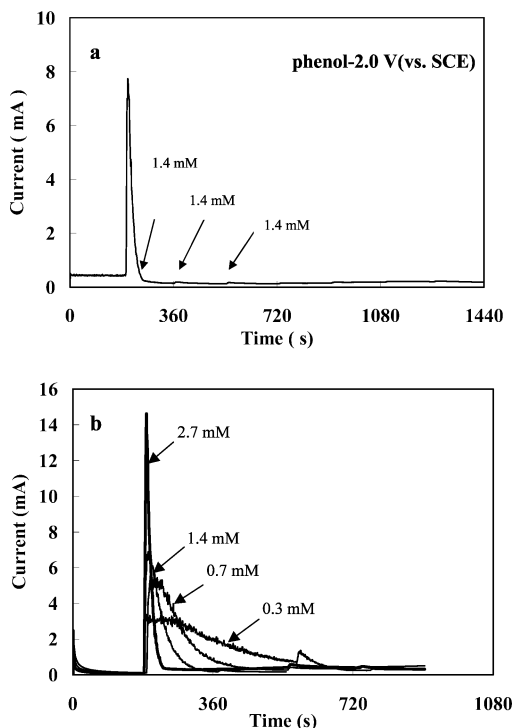
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Figure 1. (a) Typical chronoamperometric response of BDD anode to step-by-step injection of phenol. (b) Current decay curves at various injection phenol concentrations (polarized potential 2.0 V vs SCE). The arrows indicate the concentration of phenol contained in 0.1 M Na₂-SO₄ injected into the reaction system.

Figure 2. Typical chronoamperometric response of the BDD anode to step-by-step injection of phenol (polarized potential 2.6 V vs SCE). The arrows indicate the concentration of phenol contained in Na₂SO₄ injected into the reaction system.

molecules, due to a lack of adsorption sites.[22−25] Therefore, it is difficult to assume a large accumulation of high amounts of hydroxyl radicals on the BDD surface that mediates the incineration reactions. However, the hydroxyl radicals produced may diffuse into bulk very close to the electrode and cause such reaction in the vicinity of the electrodes, as their lifetime is not enough to diffuse into the bulk of the electrolyte to cause homogeneous reactions. Therefore the previous results of other researchers showing complete combustion of organics including phenol may involve the direct electron transfer to a significant extent. However, evidence for this reaction is necessary, which is shown in this work.

If the hydroxyl radicals produced on the anode surface through water discharge mediate the electrochemical oxidation, the observed current for this pathway should be independent of the concentration of organic substrate because the water concentration is constant. However, the current corresponding to direct oxidation should be dependent on the concentration of the organic substrates. On the basis of this assumption, for elucidating whether any direct electron-transfer reaction takes place on the surface of BDD anode, a comparison experiment was made by chronoamperometric measurements of current by the step-by-step injection of phenol into the solution by polarizing the BDD anode at different potentials, 2.0 V to 4.6 V (vs SCE), respectively.

First, chronoamperometric experiments were done at an applied potential of 2.0 V as seen in Figure 1a, a sharp increase in current upon the addition of phenol followed by a rapid current decay was observed when the BDD anode was polarized at 2.0 V (vs SCE), at which water cannot be discharged on the BDD electrode. Further addition of phenol did not lead to current increase anymore, indicating that the electrode surface was highly and very rapidly passivated by the deposition of a polymer film that prevents further oxidation. Figure 1b shows
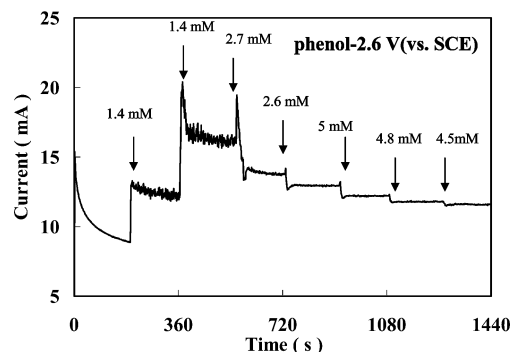
the current decay curves recorded for additions of different initial amounts of phenol. It can be seen that the passivation is delayed with the lowering of the initial concentration of phenol, which is a characteristics of polymer growth controlled by diffusion of species to the electrode rather than by an electrochemical step.

However, the situation is slightly different when the applied potential was increased to 2.6 V vs SCE, which is the potential where water can be discharged and hydroxyl radical can be generated. As seen in Figure 2, for the first two additions, the current increased with increasing concentration, but gradually decreased with further additions of phenol, indicating that the oxidation reaction is controlled by an electrochemical step rather than by diffusion of species to the electrode.

A reasonable interpretation for the different behaviors for polarization potentials at 2.0 and 2.6 V (vs SCE) is that, when the oxidative potential increase to 2.6 V (vs SCE), due to the discharge of water, hydroxyl radical-mediated reactions also participate in phenol oxidation in addition to direct electron-transfer reaction,[19] so that the polymerization process is hindered to some extent, causing a decrease in electrode fouling. However, due to the domination of direct electron transfer at high phenol concentrations, the current gradually decreased with further injections of phenol as a result of the surface coverage by electropolymerized film on the BDD anode. As a result, the BDD anode was completely passivated and the current of the direct electron-transfer reaction has dropped.

Additionally, a typical SEM image of the surface, after polarizing the BDD anode at 2.6 V (vs SCE) in the phenol solution, is shown in Figure 3. It can be seen that the polymer film was clearly identified as a rough surface in comparison to a clean and flat surface of the BDD electrode without polymer film.

However, the situation turned more interesting when the electrode was polarized at a potential of 4.6 V (vs SCE), where hydroxyl radicals are expected to form with high yield due to the increase in the rate of water discharge. Surprisingly, an increase of the steady-state current was observed, with an increasing concentration of phenol even at this high potential. As mentioned before, if the reaction is completely controlled by the hydroxyl radical mediation, the current should be independent of phenol concentration. However, the present observation suggests the presence of direct electron transfer to a significant extent in addition to hydroxyl-mediated oxidation that is expected in this potential region. The fact that the electrode is not fouled indicates that the reaction pathway toward incineration has been facilitated due to faster reaction rates for the formation of phenoxide radicals and the subsequent forma-
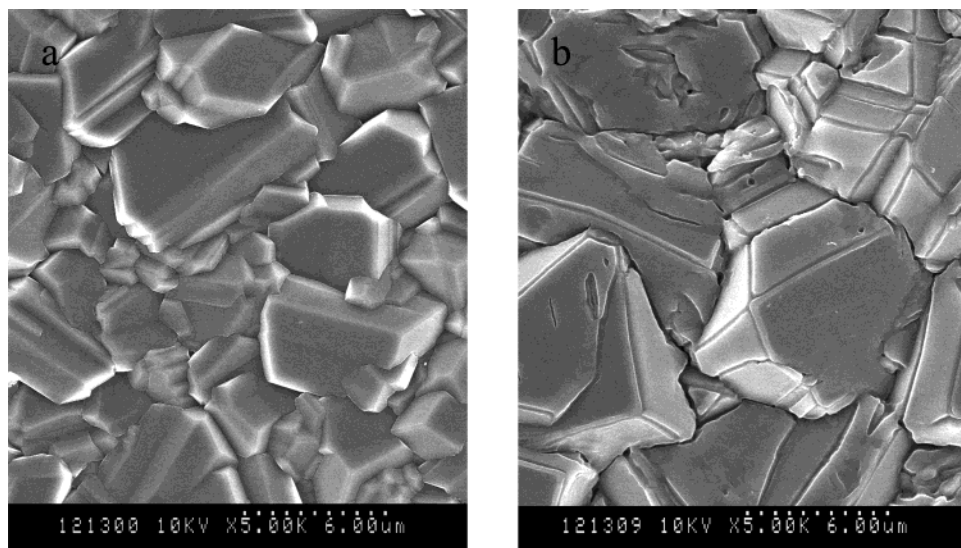
Figure 3. SEM image of the BDD electrode displaying the surface of electropolymerized film of phenol (a) before electrolysis, and (b) after electrolysis at 2.6 V (vs SCE) for 30 min.
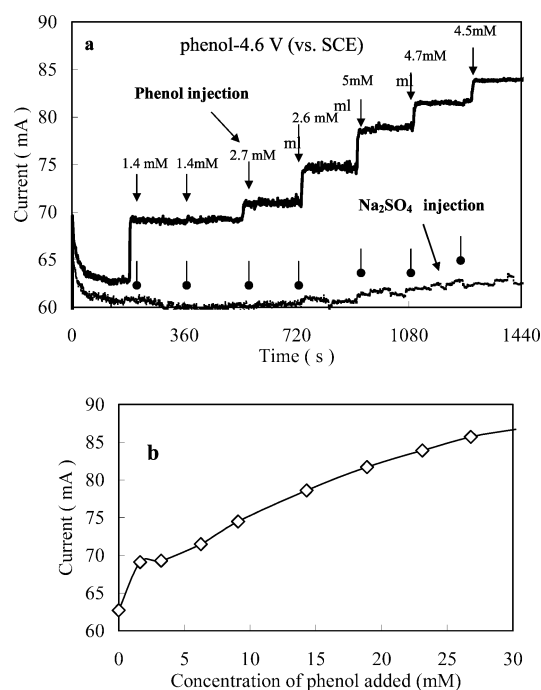

Figure 4. (a) Typical chronoamperometric response of BDD anode to step-by-step injection of phenol in 0.1 M Na_2SO_4 (polarized potential 4.6 V vs SCE,). The arrows indicate the concentration injected into the reaction system of phenol contained in 0.1 M Na_2SO_4 (→), and 0.1 M Na_2SO_4 (─●) containing no phenol. (b) A plot shows the corresponding current increases as a function of phenol concentration.

tion of phenoxonium ions at high potential rather than polymerization. At lower potentials, the phenoxide radicals rapidly undergo polymerization before oxidizing to the phenoxonium ion; however, with increasing potential, the rate of formation of this ion is facilitated due to the faster charge transfer. On the other hand, the current increase has dropped off with increasing concentrations of phenol as shown in Figure 4b. This behavior suggests that the direct electrochemical oxidation pathway involves surface-sorbed species that saturate the available surface sites on the BDD anode at high phenol concentrations.

From the mechanism point of view, the direct electron-transfer involves a proton loss while the mediated oxidation involves

the attack of nucleophiles such as hydroxyl radicals and other activated intermediates produced from water and the supporting electrolyte, respectively. According to Comninellis et al.,[14] electrolysis at high anodic potentials causes complex oxidation reactions involving electro-generated hydroxyl radicals and an electrogenerated oxidant such as peroxodisulfuric acid when sulfuric acid was used as the supporting electrolyte. In our case, the electrolysis of supporting electrolyte (Na_2SO_4) is probably less pronounced, as no significant increase in the current was observed with an increasing number of additions of 0.1 M Na_2SO_4 of supporting electrolyte (Figure 4a). This finding favors the explanation of the direct electrooxidation process of phenol on the BDD surface, indicating the stability of Na_2SO_4 as the supporting electrolyte in the present experimental condition.

To obtain further understanding of the direct electrochemical oxidation pathway occurring on the surface of the BDD anode, experiments were also done using a simple organic compound, sodium formate, which does not form an electropolymized film on the electrode surface at these potentials. The direct oxidation of formate involves two electrons to produce CO_2. Figure 5 shows a chronoamperometric response recorded for successive additions of sodium formate to 50 mL of 0.1 M Na_2SO_4 solution in the cell with the BDD polarized at different applied potentials 2.2 and 3.0 V (vs SCE). It can be seen that, the same as for the phenol at higher polarized potential (4.6 V vs SCE), an increase in the current with increasing concentrations of sodium formate was observed at both polarized potentials examined. Similar to the phenol case, the current increase has saturated at high formate concentrations, indicating the saturation of active adsorption sites on the BDD surface at high concentrations. At higher potentials, the saturation occurs at a much higher concentration due to the faster reaction of the adsorbed species. These results, together with those of phenol, suggest the involvement of the adsorption of organic substrates in the oxidation reactions. Although, an as-grown BDD with high hydrogen coverage is known to be inert to adsorption of polar molecules,[23−24] the adsorption may be facilitated at high applied potentials (in the water discharge region) that turns the surface oxygen terminated.[26] Hence, in accordance with all these experimental facts, present results clearly indicate that the direct electrochemical oxidation pathway occurs on the surface of the BDD electrode.
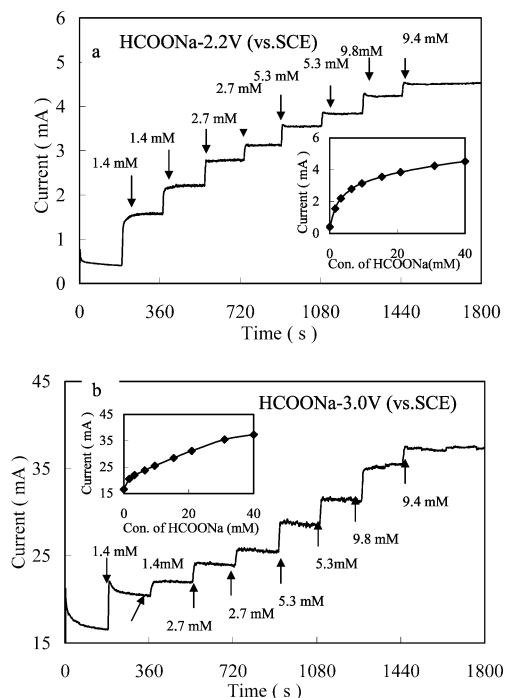
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Figure 5. Typical chronoamperometric response of BDD anode to step-by-step injection of sodium formate (polarized potential (a) 2.2 V; (b) 3.0 V (vs SCE) containing 0.2 M sodium formate in 0.1 M Na_2SO_4). The arrows indicate the concentration injected into the reaction system of formate contained in 0.1 M Na_2SO_4. Inserts show the corresponding current increases as a function of formate concentration.

TABLE 1: Degradation of Phenol and Formate by Direct Oxidation Pathway at the BDD Electrode

	applied potential (V vs SCE)	initial incineration rate (mM/min)	current increase (mA/mM)	direct oxidation rate (mM/min)	direct oxidation %
phenol	4.6 (2e)	0.011	6.51	0.00202	18.3
	2.6 (1e)	0.007	3.57	0.0022	31.7
formate	3.0 (2e)	0.0017	2.85	0.00089	52.1
	2.2 (2e)	0.00024	0.60	0.00019	79.1

Table 1 summarizes the percentage of organic substrate degradation that proceeds through the direct oxidation pathway. While two-electron oxidation was assumed for formate oxidation, both one-electron and two-electron oxidation reactions were assumed for phenol at 2.6 and 4.6 V, respectively, on the basis of the fact that electrode fouling was observed for phenol at 2.6 V, indicating the formation of one-electron products (phenoxy radicals) that quickly form a polymer rather than undergoing second-electron oxidation to the phenoxonium ion (see Scheme 1). With this assumption, the contribution of direct oxidation of phenol was found to be 31.7% and 18.3% at 2.6 and 4.6 V, respectively. The lower value at higher potential is due to the increasing contribution of hydroxyl radical-mediated oxidation. The value of 18.3% at 4.6 V is the maximum possible contribution, because it may become smaller if the four-electron oxidation to quinone is assumed. Another interesting point is that the contribution of direct oxidation is much higher for formate, indicating the higher adsorption of formate at the BDD surface.

3.2. Bulk Electrochemical Incineration of Organic Pollutants (COD removal). *3.2.1. Comparisons of Anodic Materials.* Despite the fact that the electrochemical stability of the BDD has been well-studied, only a limited number of investigators have attempted to compare the performance of the BDD with other traditional anodes.[9] In the present study, first, three
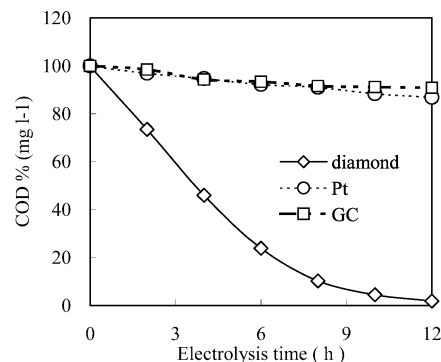

Figure 6. Comparison of different anode materials for the electrochemical incineration of phenol in terms of COD removal (phenol concentration = 7.5 mM, initial COD = 1620 mg L^{-1}). Experimental conditions: the concentration of Na_2SO_4 supporting electrolyte = 0.1 M, current density = 15 mA cm^{-2}.

kinds of electrodes were compared for their effectiveness to achieve electrochemical incineration of phenol (initial COD = 1620 mg L^{-1}) in a stirred solution of 0.1 M Na_2SO_4 as supporting electrolyte at ambient temperature under galvanostatic conditions (ca. 15 mA cm^{-2}, initial potential is about 4.6 V vs SCE). The results are shown in Figure 6 in terms of COD removal efficiency.

Electrolysis at the glassy carbon (GC) electrode caused a severe deterioration under the applied current density during the formation of a nonadherent oxidized layer and exfoliation, and only 9% COD (Figure 6) removal efficiency was achieved with a GC electrode after a 12 h electrolysis period. For the Pt electrode, a brownish yellow film on the surface was observed, which indicated that a complete oxidation degradation of phenol to CO_2 at the Pt electrode is difficult due to the passive film. The removal of COD was in the range of 13% after electrolysis for 12 h. In contrast to GC and Pt electrodes, it is apparent that the BDD electrode nearly destroyed almost all of the organic matter under virtually identical conditions. The maximum COD removal efficiency of about 96% was obtained for the BDD electrode, which was satisfactory for the practical applications.

3.2.2. Electrochemical Intermediate and Proposed Reaction Pathway. The difference in behavior between BDD, Pt, and GC electrodes are also deducible from different intermediates observed during electrolysis at these three kinds of electrodes. The phenol concentration was monitored by HPLC during the course of electrolysis, and typical results are shown in Figure 7. As can be observed in Figure 7b, for the Pt electrode, the phenol appears to degrade fairly rapidly, the peak height of phenol decreased to 30% of its initial concentration (Figure 7a) after 8 h electrolysis; however, the phenol is not oxidized completely to CO_2. All partial oxidation products were not identified; however, maleic acid was found to be a major product by comparison with data obtained with standard samples. This result is a direct consequence of the active nature of the Pt electrode and is in line with the observations of other authors.[27−28] On the contrary, almost only a single chromatographic peak was observed, which resulted from un-decomposed phenol with almost a negligible amount of intermediates (only a very small peak) after 3 h of electrolysis as shown in Figure 7c, indicating that almost complete electrochemical incineration of phenol was achieved at the BDD under present electrolysis conditions. A very small peak appearing in the chromatographic graph is due to a maleic acid. This fact indicates that an aromatic ring cleavage reaction is favored under this experimental condition on the BDD electrode, which is the reason for the high incineration efficiency observed in Figure 6. These short chain

SCHEME 1: Reaction Pathways for Phenol Electrooxidation in Aqueous Phase
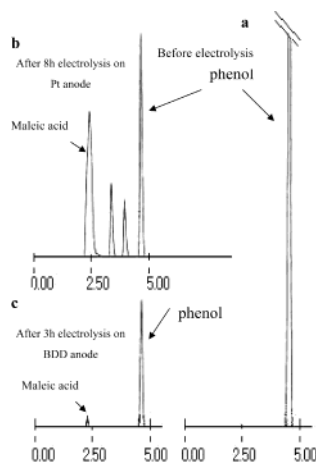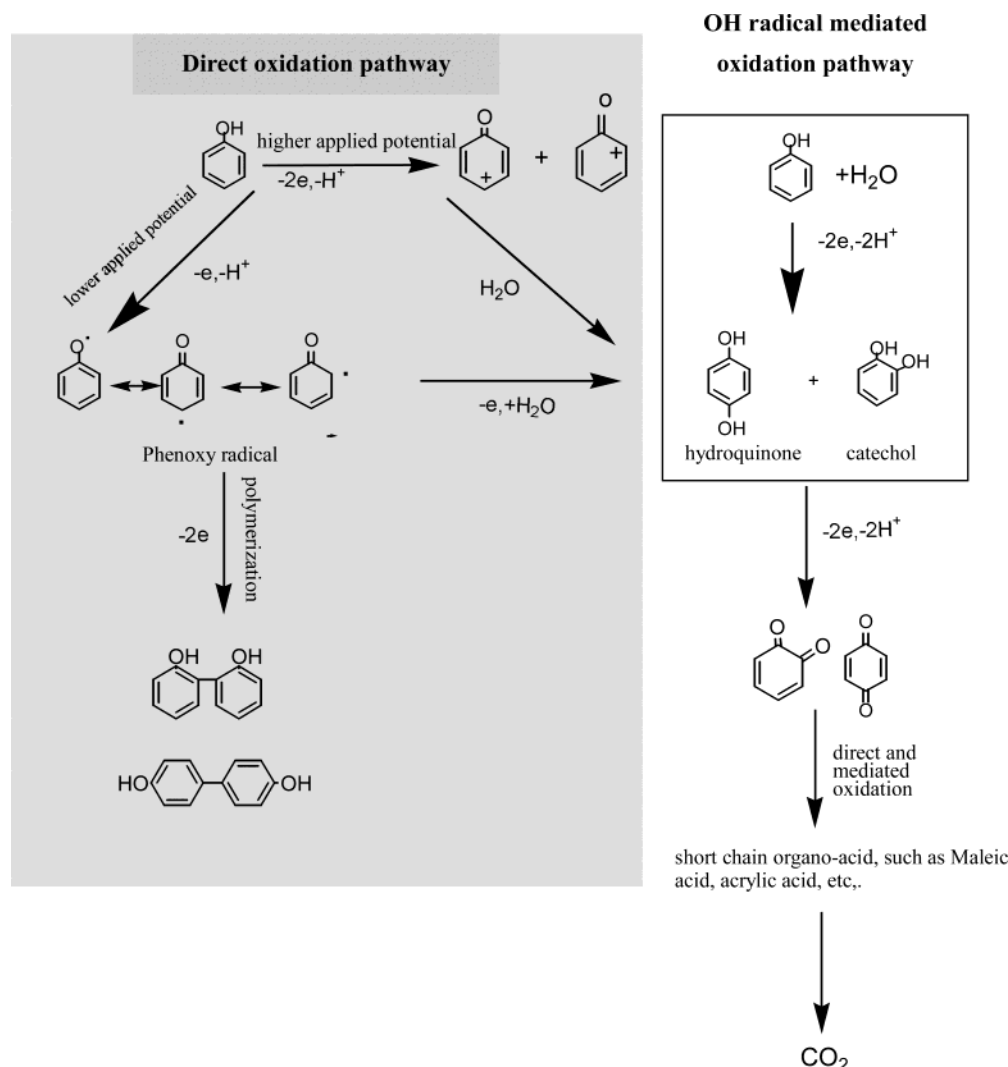

Figure 7. Chromatographic results of the phenol solution (2.5 mM) before (a) and after (b and c) electrolysis at the Pt (b) and the BDD (c) electrode.

Taking all the above facts into account, the scheme proposed for the phenol electrochemical incineration on the BDD anode is as follows (Scheme 1): For the initiation of hydroxylation of phenol to hydroquione and catechol as the initial step, it is assumed that both dihydroxyl benzenes follow the same oxidation route.[29] Formation of dihydroxyl benzene was assumed to occur through both direct and mediated oxidation. Further two-electron oxidation lead to the formation of quinone as the intermediate. However, as shown in Figure 7b, quinone was not detected by use of the BDD anode at higher potential (such as 4.6 V vs SCE) and only traces of maleic acid were detected, even in the beginning of electrolysis under our experimental conditions. This fact can be explained by the fact that hydroquinone or catechol are easily oxidized to the ring destruction products and the rate of oxidation can be fast to achieve the mineralization on the BDD anode at higher potential.

4. Conclusion

As far as we know, the present work is the first in-situ observation for direct electron transfer reaction on the BDD surface. In this paper, we have pointed out that there is strong evidence to believe that electrochemical incineration might be partly attributed to the direct electrochemical oxidation pathway on the surface of the BDD anode. The extent of degradation of phenol and formate due to direct oxidation and hydroxyl radical-

acids must be responsible for the observed residual COD during electrolysis. Finally, these short acids were easily destroyed, resulting in a complete oxidation of phenol. From the point of view of the reaction mechanism discussed above, we can conclude that the direct oxidation pathway (i.e., electron transfer) at the BDD is essentially a surface reaction at such high current density (initial potential is about 4.6 V).

mediated oxidation were quantified by amperometric measurements. The extent of direct oxidation was found to decrease with increasing potentials due to the competing hydroxyl radical-mediated reactions. The extent of direct oxidation for formate was found to be higher than that for phenol, indicating the probability of higher adsorption of formate on the oxygen-terminated diamond surface. The results of the present investigation may be important for controlling electrolysis conditions to achieve better incineration and stability with high current efficiency.

Finally, the BDD was shown to be a superior electrode, in comparison to Pt and GC, in terms of high pollutant removal rates and negligible intermediates. The complete set of data collected on the optimum conditions of electrochemical incineration of organic pollutants will be published elsewhere.

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