

Electrochemical Degradation of Phenol and 2-Chlorophenol Using Pt/Ti and Boron-Doped Diamond Electrodes

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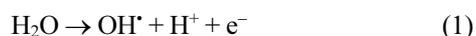
To test the efficiency of the BDD electrode for complete mineralization of organic wastewater, phenol and 2-chlorophenol (2-CP) were treated electrochemically with both an active Pt/Ti electrode and a nonactive boron doped diamond (BDD) electrode, respectively, in neutral aqueous medium. Aqueous solutions of both phenol and 2-chlorophenol were treated electrochemically using an in-house fabricated flow through electrochemical cell (FTEC). The experimental variables included current input, treatment time, and the flow rate of the solutions. Depending on the magnitude of the applied current and reaction time, the compounds were either completely degraded or partially oxidized to other intermediates. Removal efficiencies reached as high as 93.2% and 94.8% both at the Pt/Ti electrode and BDD electrode, respectively, at an applied current of 200 mA for a 3.0 hr reaction and a flow rate of 4 mL/min. The BDD electrode was much more efficient for the complete mineralization of phenol and 2-chlorophenol than the Pt/Ti electrode.

Key Words : Electrochemical degradation, Phenol, Pt/Ti electrode, Boron doped diamond electrode

Introduction

The removal of organic contaminants from organic wastewater by electrochemical treatment has been a subject of great interest because large amounts of chemicals need not be added to wastewater or to feed O₂ to cathodes without secondary pollution, and fewer accessories are required. Aqueous solutions of phenol and 2-chlorophenol are frequently used as model compounds for organic pollutants, because phenolic compounds are major organic pollutants in industrial waste and are very difficult to treat using conventional methods.¹⁻⁶ The photochemical methods, which shows the photocatalytic behavior, also have been applied to the oxidation of the phenols using the TiO₂ electrodes.^{7,8} However, these methods need the additional photocatalyst, such as TiO₂.

The anode materials used not only influence process performance but control the final oxidation products and current efficiency in the case of electrochemical treatment. Available methods for the treatment of chlorophenol waste materials include the use of different kinds of anodes including a porous felt, titanium coated with SnO₂, IrO₂,⁹ PbO₂, and boron-doped diamond.¹⁰ Using these materials, the oxidation of organics is mediated and performed *via* hydroxyl radicals that are electrogenerated on the electrode surface from water discharge (Eq. 1),^{11,12}



and/or by direct oxidation of hydroxyl ions (Eq. 2).



Metal oxides are not acceptable for wastewater treatment due to their inherent toxicity and limited service-life, in spite

of their advantages, which include the fact that they are economical and the adsorption of the products to the electrode surface are minimized. However, the boron doped diamond (BDD) electrode is quite stable, has a wide potential window for water discharge, and its toxicity is minimal. As a result, it is a promising candidate for use in the treatment of organic waste water.²

Recently, it has been shown that on some anodes, oxidation of organics can occur only under conditions of simultaneous O₂ evolution.^{13,14} A generalized mechanism has also been proposed in which complete oxidation of organics to CO₂ is achieved on “non-active” electrodes, which do not participate in the oxidation, due to the formation of hydroxyl radicals and selective oxidation occurs on “active” electrodes, which participate in the oxidation, due to the formation of a higher oxide.¹⁵⁻¹⁷ The BDD electrode is a typical nonactive electrode, whereas thermally prepared Pt/Ti electrode may serve as an active electrode for waste water treatment.¹⁸

In the present work, to test the feasibility of using the BDD electrode for complete organic wastewater treatment, phenol and 2-chlorophenol (2-CP) were treated electrochemically with both an active Pt/Ti electrode and a nonactive BDD electrode, respectively. For the electrochemical treatment of aqueous phenol and 2-chlorophenol solutions, the experimental variables including current input, reaction time, and flow rate were optimized. The effect on pH on the degradation of benzoquinone was investigated in our previous work, therefore, the pH of the test solution was maintained as neutral with 0.1 M KNO₃ electrolyte.¹⁹ The electrochemical degradation products of phenol and 2-chlorophenol were identified by HPLC. The electrochemical behavior of the BDD and the Pt/Ti was compared under identical experimental conditions in order to study the complete minerali-

zation of phenol and 2-chlorophenol.

Experimental

Phenol and 2-chlorophenol (Aldrich, USA) were used as purchased. A 0.1 M KNO_3 solution (MERCK, Germany) was used as the electrolyte. Both a Pt/Ti electrode and a BDD electrode (14×44 mm) were used as a working electrode, respectively. The counter electrode was a 14×44 mm Cu plate. The Pt/Ti electrode have been prepared by the Pt thin film coating on the Ti substrate using the rf sputtering at 400 °C. The BDD (synthetic boron doped diamond film on conducting p-Si substrate) electrode was used as purchased from Adamant Technologies Co. (Switzerland).

The intermediates and final products produced during the electrochemical treatment were identified by HPLC (Waters, Alliance, USA) using a C18 column at 25 °C and a UV detector set at 210 nm. A 5.0×10^{-2} M solution of monobasic potassium phosphate was used as the mobile phase. The products were identified by comparing the chromatograms of authentic standards. Standard materials for HPLC, oxalic acid, succinic acid, maleic acid, and hydroquinone were purchased from Supelco Co. (USA). The efficiency of complete degradation was determined by a TOC (Shimadzu, 5000A, Japan) analysis. All aqueous solutions were prepared with purified distilled water (Milli-Q system, 18 $\text{M}\Omega\cdot\text{cm}$). Both phenol and 2-chlorophenol at 30 mL of 10 mM aqueous solution were treated electrochemically by a Potentiostat/Galvanostat (Model KST-P1, Kosentech Co. South Korea) using an in-house fabricated flow through electrochemical cell (FTEC) shown in Figure 1. The maximum applicable current of the electrochemical system used in this

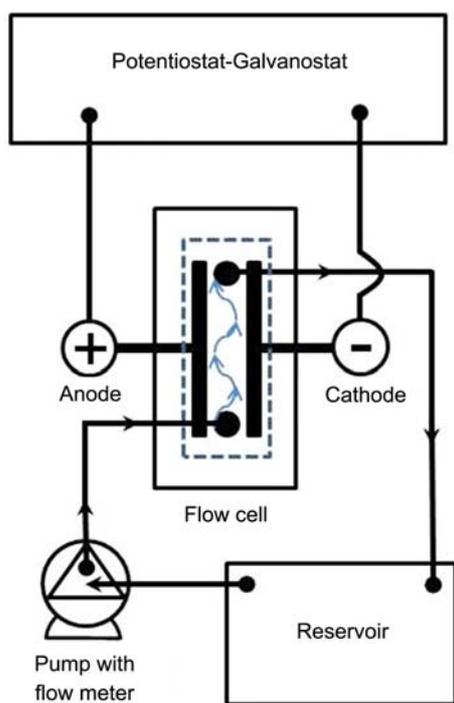


Figure 1. Schematic of the in-house fabricated flow through electrochemical cell (FTEC).

experiment was 200 mA. The reactant solution was circulated using a Master Flex[®] L/S Micro pump (Cole-Parmer Instrument Company, USA) during the electrochemical treatment.

Results and Discussion

Electrochemical Treatment of Phenol and 2-Chlorophenol at Pt/Ti Electrode. To optimize the applied current, 30 mL of 10 mM aqueous solutions of phenol and 2-chlorophenol were treated electrochemically by the varying current in the range of 20-200 mA using a FTEC at a flow rate of 4.0 mL/min using the Pt/Ti electrode. Figure 2(a) shows the degradation efficiencies for the phenol (a) and 2-chlorophenol (b) solutions as a function of applied current for a 1 hr treatment. The efficiencies of the electrochemical treatments were calculated from HPLC peak areas. The efficiency increased with increasing applied current. For the case of the 1 hr electrochemical treatment of the phenol

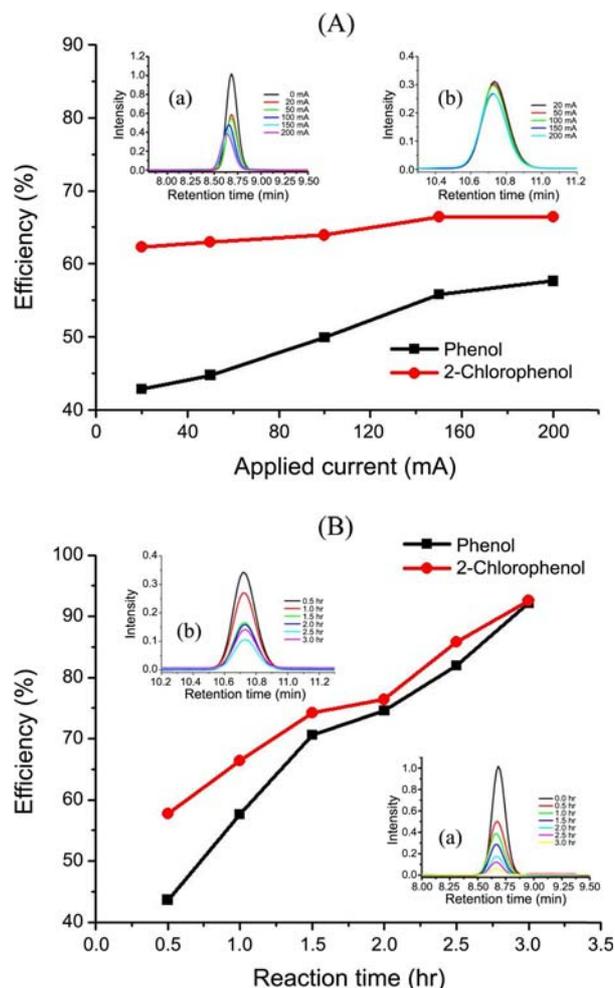


Figure 2. (A) Electrochemical degradation efficiencies for phenol (■) and 2-chlorophenol (●) as a function of applied current for a 1 hr treatment with a Pt/Ti plate electrode. (B) Electrochemical degradation efficiencies of phenol (■) and 2-chlorophenol (●) as a function of electrochemical treatment at an applied current of 200 mA with a Pt/Ti plate electrode.: HPLC chromatograms of the phenol(a) and 2-chlorophenol(b).

solution, the degradation efficiency was 57.7%, even when an applied current of 200 mA was used. The 2-chlorophenol solution was also electrochemically treated using the same procedure as was used for the phenol solution, to investigate the effect of a chloro-group on the process. For an 1 hr treatment, the degradation efficiencies were higher than those for phenol. This can be attributed to the electron withdrawing effect of the chloride group on the phenyl ring, which facilitates the production of OH radicals from the phenol moiety preceding the degradation process. Even for an 1 hr treatment of 2-chlorophenol when an applied current of 20 mA was used, the degradation efficiency was 62.4%, indicating that the effect of a chloro-group influences the initial process in the electrochemical treatment of 2-chlorophenol.

The treatment time is also a factor in the electrochemical treatment of solutions of phenol and 2-chlorophenol.²⁰ The electrochemical treatments were carried out by varying the treatment time between 0.5 hr and 3 hr at an applied current of 200 mA using a Pt/Ti electrode. Figure 2(b) shows the degradation efficiencies as a function of electrochemical treatment time at an applied current of 200 mA for the phenol (a) and 2-chlorophenol (b) solutions, respectively, using a Pt/Ti electrode. The peak area increased with increasing treatment time. For the 0.5 hr electrochemical treatment of phenol, the degradation efficiency was 43.2%, however, this value was increased to 93.2% for a 3 hr process. The degradation products produced from phenol were identified by HPLC were found to be low molecular weight aliphatic acids, maleic, succinic, fumaric, oxalic, acetic, and formic acid. Other products, including hydroquinone and benzoquinone were also identified in cases of some of the treatment conditions.² As reported in our previous study² and in other studies,^{21,22} aromatic by-products including hydroquinone and benzoquinone are formed in the first step in the degradation process and these are then further degraded to organic acids, such as fumaric acid, succinic acid, maleic acid, *etc.* (2nd step). In the 3rd degradation step, the higher molecular weight aliphatic compounds are degraded to lower molecular weight compounds, including oxalic acid, acetic acid, and formic acid, which are then mineralized to CO₂. For the case of the 0.5 hr treatment of 2-chlorophenol at an applied current of 200 mA, the degradation efficiency was 57.6%. The efficiency of electrochemical degradation increased with increasing processing time, and eventually reached 93.6% for a 3 hr process.

Degradation of Phenol and 2-Chlorophenol using a BDD Electrode. Figure 3(a), shows the degradation efficiencies of phenol (a) and 2-chlorophenol (b) as a function of applied current for a fixed treatment time of 1 hr using a BDD electrode. The same procedure was used for the electrochemical degradation of both phenol and 2-chlorophenol with the BDD electrode as was followed for the Pt/Ti electrode. The electrochemical degradation efficiency of phenol as a function of applied current for an 1 hr electrochemical treatment increased with increasing applied current. At an applied current of 20 mA, the electrochemical de-

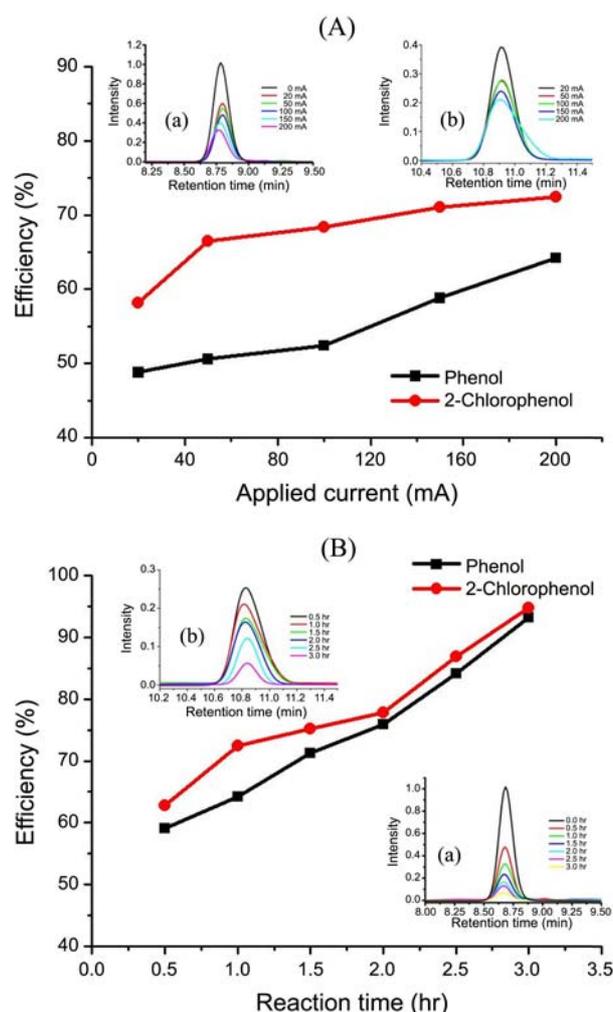


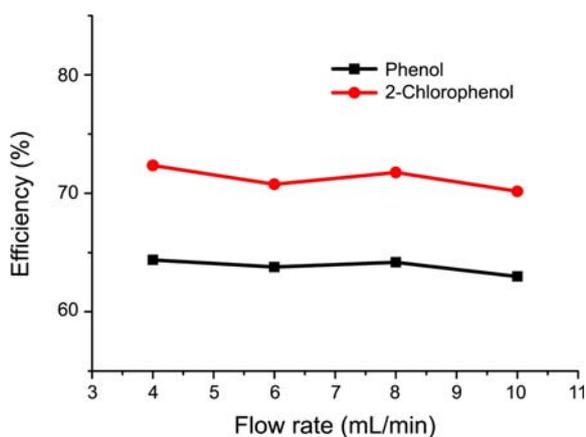
Figure 3. (A) Electrochemical degradation efficiencies for phenol (■) and 2-chlorophenol (●) as a function of applied current for a 1 hr treatment with a BDD electrode. (B) Electrochemical degradation efficiencies of phenol (■) and 2-chlorophenol (●) as a function of electrochemical treatment at an applied current of 200 mA with a BDD electrode. HPLC chromatograms of the phenol (a) and 2-chlorophenol (b).

gradation efficiency was 48.2%, however, it increased to 64.8% for an applied current of 200 mA. The calculated treatment efficiency for 2-chlorophenol was 58.2% at an applied current of 20 mA. The electrochemical degradation was 72.6% for an 1 hr process at an applied current of 200 mA, a value that is higher than the corresponding value for phenol. This also can be explained by the electron withdrawing effect of the chloro-group. The results show that the degradation of both phenol and 2-chlorophenol with a BDD electrode are much more efficient than that for the Pt/Ti electrode.

To obtain a higher treatment efficiency, the electrochemical degradation of phenol and 2-chlorophenol were carried out by varying the treatment time from 0.5 hr to 3.0 hr at an applied current of 200 mA with the BDD electrode. Figure 3(b) shows the effect of electrochemical treatment time on the degradation of phenol(a) and 2-chlorophenol (b)

Table 1. TOC results of electrochemical degradation efficiency for the CO₂ generation from the phenol and 2-chlorophenol depends on the reaction time (0.5-3.0 hr) at a constant applied current of 200 mA

Degradation time (hr)	Pt/Ti plate electrode				BDD electrode			
	Results of TOC (ppm)		Degradation yield (%)		Results of TOC (ppm)		Degradation yield (%)	
	Phenol	2-Cl	Phenol	2-Cl	Phenol	2-Cl	Phenol	2-Cl
0.0	734.5 ± 1.2	899.2 ± 0.9	-	-	734.5 ± 1.2	899.2 ± 0.9	-	-
0.5	490.6 ± 0.9	466.3 ± 1.0	33.2	48.1	492.0 ± 0.7	389.5 ± 0.8	33.0	56.3
1.0	477.5 ± 1.1	389.3 ± 1.2	35.0	53.3	353.3 ± 0.9	367.2 ± 1.0	51.9	59.2
3.0	297.5 ± 1.4	419.5 ± 1.3	59.5	56.8	148.5 ± 1.2	145.4 ± 1.1	79.8	83.6

**Figure 4.** Electrochemical degradation efficiencies of phenol (■) and 2-chlorophenol (●) as a function of flow rate (10-40 mL/min) at a constant applied current (200 mA) for a 1 hr treatment with a BDD electrode.

at an applied current of 200 mA. At a reaction time of 0.5 h, the electrochemical degradation of phenol was 59.2%. The electrochemical degradation increased with increasing treatment time. A degradation efficiency of 93.7% was found for the case of a 3hr reaction. For the 0.5 hr electrochemical treatment of 2-chlorophenol, the calculated degradation efficiency was 62.8%. The 2-chlorophenol was continuously degraded to low molecular weight aliphatic acids and CO₂ throughout the 3 hr treatment period, with an efficiency of 94.8%.

Compare to the Pt/Ti electrode, the BDD electrode is much more efficient for the electrochemical degradation of both phenol and 2-chlorophenol, especially in the initial phase of the reaction. The effect of the flow rate of the test solution on electrochemical degradation was studied by varying the flow rate within the range of 4-10 mL/min using the BDD electrode. As shown in Figure 4, no significant differences were found in the treatment efficiencies for both phenol and 2-chlorophenol using 30 mL of a 10 mM aqueous solution at an applied current of 200 mA for a 1 hr reaction.

Mineralization of Phenol and 2-Chlorophenol. The partial mineralization of phenol and 2-chlorophenol to CO₂ was observed for all the electrochemical processes. The mineralized phenol and 2-chlorophenol both at the BDD and Pt/Ti electrode were determined by a TOC analysis,

separately. As shown in Table 1, the mineralization efficiencies for both phenol and 2-chlorophenol using the BDD electrode were about 1.4 times higher than the corresponding values for the Pt/Ti electrode, again indicating that the BDD electrode is much more efficient for the complete degradation of phenolic compounds. This can be explained the complete oxidation of organics to CO₂ by generated hydroxyl radicals on 'non-active' BDD electrode and the selective oxidation on the thermally prepared Pt/Ti thin-film electrode.^{15,18,23}

Conclusion

Using the BDD electrode and the Pt/Ti electrode, electrochemical degradation was successfully accomplished for both phenol and 2-chlorophenol. The optimized conditions for the electrochemical treatment of both phenol and 2-chlorophenol was an applied current of 200 mA and a 3 hr processing time. Under optimized conditions, 93.7% of the phenol was degraded to low molecular weight aliphatic acids and 94.8% of the 2-chlorophenol was similarly degraded using the BDD electrode. The mineralization of phenol and 2-chlorophenol using the BDD electrode was compared with the corresponding values for the Pt/Ti electrode by TOC analysis. The BDD electrode was much more efficient for the mineralization of phenol and 2-chlorophenol than the Pt/Ti electrode.

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