p-Benzoquinone Anodic Degradation by Carbon Black Diamond Composite Electrodes

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ABSTRACT

In this work, *p*-benzoquinone (p-BQ) electro-degradation in three carbon black diamond (CBD) composite electrodes is studied under conditions of 200 mg/L initial concentration, 45 mA/cm^2 applied current density, pH 3, and 0.25 M Na_2SO_4 as a supporting electrolyte. The performance of the CBD electrodes was compared with that of a platinum electrode. Results showed that the optimal p-BQ degradation, COD removal efficiency, and current efficiency may be obtained from the CBD electrode containing 20% carbon black (20CBD). After 20 min of electro-degradation, p-BQ removal on 20CBD reached 96% at pH 6 and 61.5% at pH 3. However, after 180 min of p-BQ degradation, COD removal on this electrode reached 45% at pH 6 and 70% at pH 3. Increases in applied current during p-BQ electro-oxidation were related to the initial p-BQ concentration. Significant differences were observed in the solution containing 200 mg/L p-BQ as the current density was increased from 20 mA/cm^2 to 45 mA/cm^2; no such effects were observed in the solution with 1000 mg/L p-BQ.

1. Introduction

Anodic oxidation of aromatic compounds, especially toxic and refractory (i.e., resistant to biological treatment) reagents, has been extensively investigated by many researchers. Previous studies on this topic have mainly concentrated on developing efficient electrodes or selecting optimum operation conditions, including current density, solution pH, temperature, flow rate, and initial organic pollutant concentration, to achieve oxidation. *p*-Benzoquinone (p-BQ) is an important chemical with many commercial uses in the pharmaceutical and polymer industries; the compound is often used in toners and intensifiers in the photography industry, production of hydroquinone, insecticides and fungicides, and tanning agents in the leather industry [2]. Most aromatic anodic oxidation processes, such as those of phenol [4,14,16], benzene [22], aniline [19], 4-chlorophenol [3], sulfanilic acid [11], bisphenol [8], sulfanilamide [12], and chlorobenzene [21], produce p-BQ as an intermediate.

p-BQ is considered a highly toxic xenobiotic compound [20] that can cause skin necrosis and eye and respiratory tract irritation [2]. Few researchers have investigated anodic oxidation reactions of p-BQ. Pulgarin et al. [27] investigated the effects of Ti/IrO_2 and Ti/SnO_2 electrodes on the anodic oxidation of BQ and reported that the anodic material significantly affects the electro-oxidation process. Whereas using Ti/Ir O_2 electrodes accumulates carboxylic acids, using Ti/Sn O_2 electrodes causes incineration of BQ and its intermediates into CO_2. Ti/SnO_2 electrodes are also known to have short work lives [25]. Houk et al. [15] studied anodic oxidation of 100 mg/L BQ using a quaternary metal oxide anode in the absence of a supporting electrolyte; this anode proved to promote electrochemical oxidation of BQ but required 64 h to achieve the process. Yoon et al. [30] investigated incineration of 0.001 M BQ using a carbon fiber anode and reported 99.23% BQ incineration under a high current density of 175 mA/cm^2 and reaction time of 12 h; extensive accumulation of intermediates was also observed. Finally, Panizza [23] studied electro-oxidation of 2000 mg/L BQ using a BDD electrode, which showed good activity for BQ incineration.

The electrochemical properties of carbon black diamond (CBD) composite electrodes were investigated for the first time in our laboratory. The CBD electrodes presented inert surfaces and wide potential windows similar to those of BDD, particularly at 5% CB (5CBD). Unfortunately, this potential window decreased in electrodes with higher CB contents, such 40% CB (40CBD) [1], and the low conductivity of the 5CBD electrode compared with those of the 10% CB (10CBD), 20% CB (20CBD), and 40% CB (40CBD) electrodes led to its exclusion from further study. Anodic oxidation of organic chemicals, such as electro-oxidation of phenol [1], by CBD electrodes has previously been investigated; in these studies, BQ was not observed as an intermediate.

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The aim of the present work is to study the anodic incineration rate of p-BQ over the CBD electrodes. This research is the first to report the effects of varying CB content in CBD electrodes on the anodic degradation of p-BQ and compare the anodic oxidation activity of CBD electrodes with that of a platinum electrode. The effects of solution pH, current density, and initial concentration of p-BQ on the degradation rate and chemical oxygen demand (COD) decay are also investigated.

2. Experimental

2.1. Preparation of electrodes

Three electrode disks measuring 1.4 cm in diameter and with different CB contents were prepared. 10CBD, 20CBD, and 40CBD were obtained by carefully mixing 1.0 g of diamond powder (98.3% purity; average particle size, 6 nm; Sigma-Aldrich) and a precise amount of CB (99% purity; average particle size, 13 nm). The powder mixtures were mixed with 20% polytetrafluoroethylene suspension in water (60 wt%; Sigma-Aldrich) as the binder and 2 g of 1,3-propanediol (98% purity, Sigma-Aldrich). The electrode paste was kneaded carefully and then dried in an oven following the program 80 °C for 2 h, 120 °C for 1 h, 200 °C for 1 h [17], and at least 275 °C for 1 h to increase the hardness of the electrodes.

2.2. Chemicals

All solutions were prepared using ultra-pure deionised Milli-Q water. P-Benzoquinone (98%), hydroquinone (99%), phenol (99%), maleic acid (99%), H_2SO_4 (97% Pro Analysis), Na_2SO_4 (99%), oxalic acid (99%), succinic acid (99%) and formic acid (91%) were from Merck. Fumaric acid (99%) was from Fluka and acetic acid (99.6%) was from Riedel-de-Haen.

2.3. Electrochemical studies

Voltammetric experiments were carried out in a 100 mL glass cell at 25 °C. The supporting electrolyte was 0.5 M H_2SO_4. Platinum and Ag/AgCl were used as the counter and reference electrode respectively. Potential windows for CBD composite electrodes and platinum electrode were performed using Autolab Metrohm potentiostat with NOVA 1.10 software.

2.4. p-Benzoquinone degradation

For electro-degradation of p-Benzoquinone experiments, a 100 mL electrochemical cell equipped with a stainless steel cathode was used. The supporting electrolyte was 0.25 M Na_2SO_4 with 200, 500 and 1000 mg/L of p-Benzoquinone concentrations. Solution stirring was performed using a C-MAG HS 7 magnetic stirrer. The experiments were conducted with 20, 32 and 45 mA/cm^2 applied current density, constant pH 3 and pH 6 and at 25 °C. ISO-TECH programmable power supply IPS 3202 was used as source of DC current.

2.5. Analysis method

The electro-degradation of p-Benzoquinone during electrolysis was examined by high performance liquid chromatography (HPLC) using an Agilent technology 1200 series. ODS hypersil C18 column (4.6 mm × 150 mm × 5 μm) at 25 °C was used as the separation column for p-Benzoquinone and aromatic compounds using acetonitrile/ water (60/40, v/v) as the mobile phase. The injection volumes and the mobile phase flow rate were 5 μm and 1 mL/min respectively. The detection wavelength was set at 254 nm. Aliphatic acid intermediates were identified by the separation on a C18 column (3.9 mm × 150 mm × 5μm) using a mobile phase consisting of 20 mM NaH_2PO_4 solution (pH 2.7) and at 0.7 ml/min flow rate. The injection volumes were 20 μm and the detection wavelength was set at 210 nm. The samples were filtered through a 0.25 μm membrane filter. The chemical oxygen demand (COD) was measured by the dichromate method. The sample for measurement of COD was introduced into prepared solution of (0–1500 mg/L) including mercuric sulfate, H_2SO_4 and potassium dichromate and the mixture then brooded for 2 h at 150 °C in a HACH / DRB 200 thermo-reactor for COD and thermal digestions. COD concentration was measured color-metrically using an ORION A03700 spectrophotometer. Current efficiency (CE) for electro-oxidation has been estimated by COD values, using the following relationship.

$$CE(\%) = \frac{(COD_\circ - COD_t)FV}{8I\Delta t} \times 100 \qquad (1)$$

Where COD_o and COD_t are the chemical oxygen demands at times t = 0 and t (in g O_2/L), respectively, and I is the current (A), F is the Faraday constant (96487 C/mol), V is the volume of the electrolyte (L).

3. Result and discussion

The electrochemical incineration of different concentrations (200, 500 and 1000 mg/L) of p-Benzoquinone (p-BQ) at 25 °C temperature and 0.25 M Na_2SO_4 as supporting solution, current density 20–45 mA/cm^2 and pH 3 and 6 was investigated on carbon black diamond composite (CBD) and platinum electrodes.

3.1. Effects of anode material

Fig. 1 compares the electro-degradation of 200 mg/L p-BQ on the 10CBD, 20CBD, 40CBD, and platinum electrodes in aqueous solution of pH 3, current density of 45 mA/cm^2, and temperature of 25 °C. Anodic degradation on the three CBD electrodes were obviously higher than that on the platinum electrode. After 120 min of reaction, p-BQ removal efficiencies of 95.25%, 94%, 85.5%, and 67.5% were respectively obtained on the 20CBD, 10CBD, 40CBD, and platinum electrodes. During degradation, the removal efficiency of p-BQ on 10CBD was similar to that on 20CBD and higher than that on 40CBD until about 270 min of reaction; thereafter, the degradation efficiencies of all three CBD electrodes became similar. Anodic oxidation of p-BQ and its intermediates is

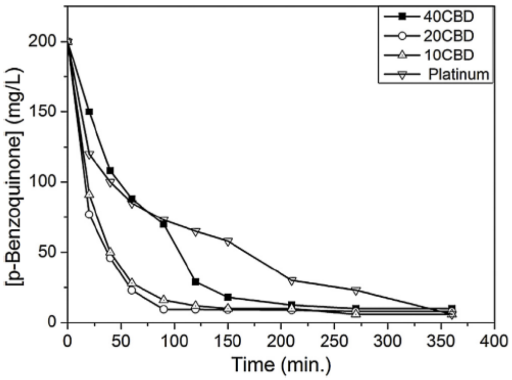

Fig. 1. Effects of electrode materials on anodic degradation of 200 mg/L of p-BQ aqueous solution at applied current density 45 mA/cm^2, pH 3 and temperature 25 °C.

initiated by hydroxyl radicals electro-generated on the electrode surface through water discharge (1.23 V vs. SHE under standard conditions) [7]. The amount of hydroxyl radicals generated on the electrode surface is related to the width of the anode potential window. Weak interaction forces between the anode surface and hydroxyl radicals also enhance the oxidative power of the electrodes [18].

Fig. 2 shows that the potential windows of the 10CBD, 20CBD, 40CBD, and platinum electrodes are 2.35, 2.4, 1.60, and 1.8 V, respectively, versus that of Ag/AgCl. The working potential window of 10CBD is clearly very similar to that of 20CBD. This finding confirms the similar degradation rates obtained on these electrodes (Fig. 1) and explains the low p-BQ anodic oxidation rate obtained on 40CBD. Platinum is generally recognized as an active electrode [26], and its potential window is wider than that of 40CBD. However, that the p-BQ electro-degradation rate on the platinum electrode is lower than that on 40CBD is attributed to more extensive interaction forces between hydroxyl radicals and the platinum electrode surface compared with those between hydroxyl radicals and the 40CBD electrode surface. 40CBD is a non-active electrode, and the inert surface of the diamond coating weakens interaction forces on the electrode surface [29]. Fig. 3 illustrates the current efficiencies obtained during the first 20 min of electro-degradation: 10CBD, 20CBD, and 40CBD yielded current efficiencies of 56%, 67%, and 58.5%, respectively. By comparison, the current efficiency of the platinum electrode was only 22.7%. Increases in reaction time decreased the current efficiencies of all of the electrodes. After 60 min of degradation, for example, a sharp drop in the current efficiency of the CBD electrodes may be observed. This decrease may be attributed to decreases in p-BQ concentration in the solution after 60 min of reaction. The

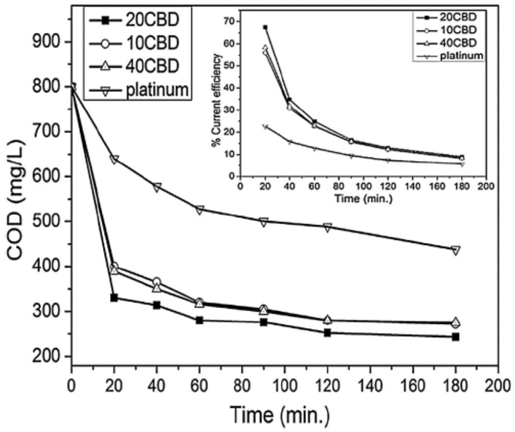

Fig. 3. Effects of electrode materials on COD decay of 200 mg/L of p-BQ aqueous solution at applied current density 45 mA/cm^2, pH 3 and temperature 25 °C.

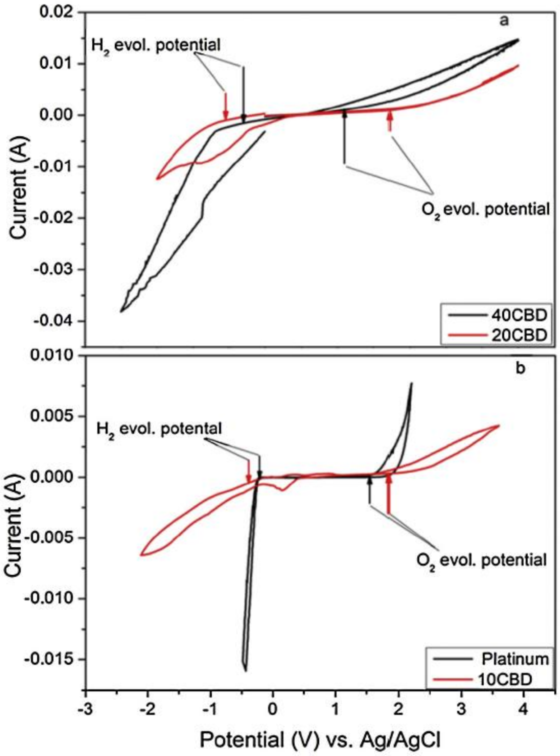

Fig. 2. Cyclic voltammetry for 20CBD and 40CBD electrodes (a) and for 10CBD and platinum electrodes (b) in an aqueous solution of 0.5 M H_2SO_4. Scan rate 0.1 mV/s and 25°C temperature.

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