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Anodic Degradation of 2-Chlorophenol by Carbon Black Diamond and Activated Carbon Composite Electrodes

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ABSTRACT

A carbon black diamond composite electrode with 20% carbon black (20CBD) and activated carbon composite (ACC) electrode were prepared and used as anodes for 2-chlorophenol electro-oxidation. The electro-oxidation behaviors of 200 mg/L 2-chlorophenol on 20CBD and ACC anodes were investigated by cyclic voltammetry in aqueous solutions of 0.5 M H_2SO_4 (pH 0.55) and 0.25 M Na_2SO_4 (pH 7). Results indicated that the 20CBD and ACC electrodes are more active at low pH than at high pH and that no oxidation peak appears on the ACC electrode. The performance of the 20CBD and ACC electrodes during degradation of 200 mg/L 2-chlorophenol was investigated in an aqueous solution of pH 3 with 0.25 M Na_2SO_4 as the supporting electrolyte and applied current density of 30 mA/cm^2. Results showed that the 20CBD electrode produced the best degradation rate, COD removal efficiency, and current efficiency. The degradation efficiencies of the 20CBD and ACC electrodes after 6 h were 96% and 82.5%, respectively. The effects of solution pH, current density, and supporting electrolyte on the performance of the 20CBD were further investigated, and results showed that higher degradation rates are obtained at lower pH and with Na_2SO_4 as the supporting electrolyte. Removal efficiency also increased with increasing current density.

1. Introduction

Chlorophenols are considered very toxic substrates with strong resistivity to biological degradation; thus, these compounds may cause serious environmental contamination [1]. 2-Chlorophenol has been classified as a priority pollutant by the Environmental Protection Agency [2]. Many uses for chlorophenols, such as in pesticides, herbicides, pharmaceuticals, dyes, and cellulose plants [1,3], have been reported. Given the strong toxicity nature and resistivity of these compounds to biodegradation, research efforts have been exerted to develop suitable techniques that can mineralize the chlorine and carbon atoms in chlorophenols. A number of techniques have been used to remove chlorophenols in wastewater, including advanced oxidation processes [4–6], adsorption [7,8], and photochemical degradation [9,10]. Among these technologies, electro-degradation of toxic and non-biodegradable chlorophenols has gained significant research attention because the technique features easy implementation, high efficiency, amenability to automation, and environmental compatibility (i.e., no requirement of chemical addition) [11]. One of the most important factors affecting the electro-degradation process is the nature of the electrode (anode) used in the process [12]. Many conventional anode materials, such as SnO_2 and PbO_2 [13], platinum [14], Sn–Sb–Ni [15], and BDD [16,17], have been tested for chlorophenol electro-degradation. Different materials, such as F-doped PbO_2 [18], Ti-based oxide [19,20], Ti/$Ru_{0.3}M_{0.7}O_2$ [21], Er-chitosan-PbO_2 [22], and Pd/PPy/foam-Ni [23], have also been improved as anodes for electro-degradation of chlorophenol substrates. Most previous studies have attempted to propose an efficient electrode with suitable electrochemical properties, long service life, and cost. Electro-oxidation of phenol, chlorophenols, and many aromatic compounds produces hydroquinone, benzoquinone, and carboxylic acid substrates. Thus, chlorophenol must be electro-oxidized beyond the benzoquinone stage for adequate treatment because these intermediates are more toxic than chlorophenols themselves [24]. Chlorophenol oxidation occurs until the aromatic ring breaks, carboxylic acids form, and most acids are mineralized to CO_2, which requires a suitable amount of quiz-free hydroxyl radicals electro-generated at the electrode surface. The amount of hydroxyl radicals generated depends on the electrochemical properties of the anode materials. Electrodes with a higher oxygen evolution potential can produce larger amounts of hydroxyl radicals and achieve suitable current efficiencies. A carbon black diamond (CBD) electrode was proposed for the first time by our laboratory for organic pollutant oxidation. This electrode had an inert surface and suitable oxygen evolution potential that depended on the CB percentage in the electrode. The potential window for a CBD electrode with 5% CB is

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similar to that of a BDD electrode; however, decreases in potential window with increasing CB percentage, such as in 40% CBD, were observed [25]. Benzoquinone electro-degradation on CBD electrodes has been investigated. Results reported for a 20% CBD electrode (20CBD) show a removal efficiency of 96.5% for 200 g/L benzoquinone after only 20 min of degradation [26]. Also, benzoquinone did not appear as an intermediate during phenol electro-degradation on the same electrode [25].

A 20CBD electrode is proposed in the present study for electro-degradation of 2-chlorophenol, and its performance is compared with that of an activated carbon composite (ACC) electrode prepared as an anode for organic substrate oxidation using a novel method. The effects of mean parameters, such as pH, current density, and supporting electrolyte, are also investigated, and a pathway and mechanism of 2-chlorophenol degradation are proposed. To the best of our knowledge, anodic degradation of 2-chlorophenol is rarely studied in the open literature and this work is the first of its kind to compare the performance of CBD and ACC for this purpose.

2. Experimental

2.1. Electrode preparation

A disk of carbon black diamond composite electrode with 20% carbon black has been prepared with surface area 2.27 cm^2. Whereas, diamond powder (98.3% purity and average particle size 6 nanometer, Sigma-Aldrich) was mixed carefully with a precise percent of carbon black Super P (99% purity, average particle size of 13 nanometer and 550 m^2/g specific surface area, Alfa Aesar). Powder mixture have been mixed with suspension (60 wt%) in water (Sigma-Aldrich) polytetrafluoroethylene as the binder and 1,3- propanediol (98% purity, Sigma-Aldrich) and then dried as described in previous work [25]. Activated carbon composite (ACC) electrodes with surface areas of 2.27 and 9.1 cm^2 were prepared by mixing 80% charcoal activated carbon (99.5% purity, average particle size 100 μm and 950m^2/g specific surface area, Sigma-Aldrich) with 20% CB. The powder mixture was added to a liquid mixture of polytetrafluoroethylene and isopropyl alcohol with a 1:2 ratio. The electrode paste was kneaded neatly and then dried in an oven using drying sequence of 100 °C for 2 h, 180 °C for 1 h, 250 °C for 1 h, and at least 350 °C for 30 min to complete the sintering process and increase the electrode hardness.

2.2. Electrochemical oxidation behavior

Voltammetric experiments were conducted in one compartment of a 100 mL glass cell at 25 °C to investigate the electrochemical oxidation behavior of 2-chlorophenol on the 20CBD and ACC electrodes. A solution of 0.5 M H_2SO_4 (97% Merck Pro Analysis) as a blank solution, and two aqueous solutions of 200 mg/L of 2-chlorophenol (99.5% Merck Pro Analysis) were prepared. One solution was composed of 0.5 M H_2SO_4 at pH 0.5, and another solution was composed of 0.25 M Na_2SO_4 at pH 7. Milli-Q water was used to prepare the solutions. A platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. Electrochemical active surface areas of the 20CBD and ACC electrodes were estimated by Chronoamperometry technique using an aqueous solution of 0.1 M KH_2PO_4 containing 5 mM $K_4Fe(CN)_6$. Effective surface area of the working electrodes were obtained by the Cottrell equation [27].

$$I = \frac{nFAD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \tag{1}$$

where I is the current (A), n is number of electrons, A is the active area of electrode (cm^2), D and C_o are the diffusion coefficient (6.20×10^{-6} cm^2/s) and bulk concentration of $K_4Fe(CN)_6$ (mol/cm^3), F is the Faraday constant (96.487 C/mol); while the remaining parameters have their usual meanings. The electrochemical experiments on 20CBD electrode and ACC electrode were performed by Autolab Metrohm potentiostat with NOVA 1.10 software.

2.3. Electro-degradation of 2-chorophenol

An electrochemical cell with 100 mL of 200 mg/L 2-chlorophenol solution, 0.25 M Na_2SO_4, 3 mg/L(0.05 M) Nacl, and 0.1 M Na_2SO_4 + 3 mg/L NaCl as the supporting electrolyte was used for 2-chlorophenol degradation experiments on the 20CBD and ACC electrodes. The experiments were conducted at applied current densities of 8, 15, or 30 mA/cm^2 and pH 3, 7, or 11 at 25 °C temperature. ISO-TECH programmable power supply IPS 3202 was used, whereas stainless steel cathode and C-MAG HS 7 magnetic stirrer were used for solution mixing.

2.4. Analysis method

The decomposition of 2-chorophenol during electrolysis was examined by high performance liquid chromatography (HPLC) using an Agilent technology 1200 series. C18 column (4.6 mm × 250 mm × 5 μm) at 20 °C was used as the separation column for 2-chlorophenol, hydroquinone, benzoquinone and other aromatic compounds. The eluent was used 60% acetonitrile/ 39.9% water + 0.1% H_2PO_4 (v/v), the injection volumes were 20 μL and eluent flow rate was 1 mL/min. The detection wavelength was set at 280 nm. Aliphatic acid intermediates were identified by using the mobile phase 25% methanol/10 mM NaH_2PO_4 solution (pH 2.7) and 0.7 ml/min flow rate. The injection volumes were 10 μL and the samples were filtered through a 0.25 μm membrane filter. Gas chromatography coupled with mass spectrometry (GC/MS) was used to identify of the aliphatic acids that were generated by the 2-chlorophenol degradation. Samples were esterified and then extracted as describe by Li et al. [28].The GC/MS (HP6890, Agilent) used a capillary column (HP-624, 25.0 m × 200 mm × 1.12 mm, Agilent) followed by detection with an MS (Netwaik 5973,Agilent). The temperature program starts at 70 °C and rises at a rate of 20 °C/min until to 260 °C. Holding time was 2 min for each increment. Helium was used as the carrier gas with constant flow rate of 54 ml/min and sample injection sample was 1 ml. The chemical oxygen demand (COD) was measured by the dichromate method. The suitable sample for measurement of COD was introduced into prepared solution of (0–1500 mg/L) and (0-150 mg/L), including mercuric sulfate, H_2SO_4 and potassium dichromate and the mixture was 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.

$$CE(\%) = \frac{F.V}{8.I.\Delta t}(COD_{\circ} - COD_t) \times 100 \tag{2}$$

Where $COD_{\circ}$ and COD_t are the chemical oxygen demands at times t = 0 and t (in gO_2/L), respectively, and I is the current (A), F is the Faraday constant (96487C /mol), V is the volume of the electrolyte (L) and 8 is the equivalent mass of oxygen (g eq^{-1}).

3. Results and discussion

3.1. Anodic oxidation behavior of 2-chlorophenol on the 20CBD and ACC electrodes

Prior to the electro-degradation study, the electro-oxidation behavior of 2-chlorophenol was studied on 20CBD and ACC