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Preparation and characterization of carbon black diamond composite electrodes for anodic degradation of phenol

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ABSTRACT

Carbon black diamond (CBD) composite electrodes have been prepared with different percentages of carbon black (5% (5CBD), 20% (20CBD) and 40% (40CBD) as the conductive agent. This article reports for the first time the electrochemical behavior of CBD electrodes. The electrochemical properties of these three electrodes were characterized by cyclic voltammetry in 0.5 M H_2SO_4 and at 100 mV/s scanning rate. The working potential windows of 5CBD, 20CBD and 40CBD electrodes were 3.35, 2.4 and 1.75 V vs. Ag/AgCl respectively. Anodic oxidation behavior of phenol was studied by cyclic voltammetry on CBD electrodes in aqueous solution of 0.5 M H_2SO_4, 0.5 M Na_2SO_4 and 0.5 M NaOH containing 500 mg/L phenol at 25 °C. The results indicated that the CBD electrodes were more active at low pH solution. The anodic oxidation of phenol led to the formation of passive adhesive film on CBD electrodes which reduced the peaks until a constant value of oxidation current was obtained. 20CBD electrode was selected to study the degradation of 500 mg/L phenol solution with pH 3 and pH 6 and applied current density of 50 mA/cm^2. The removal efficiency was more than 97% at pH 3.

1. Introduction

Electrochemical oxidation of organic pollutants has gained significant attention over the past two decades as a new and attractive technology. This technology is environmentally compatible due to the absence of chemical agents, and there is no tendency to produce secondary pollution [1]. The technology has reached a good state compared to other conventional technologies not only in terms of cost, but sometimes it is also more efficient and compact [2]. The material of electrode is the most important factor in this process [3,4]. Most of the investigations in organic electro-oxidation have been concentrated on the study of the parameters of anode materials and attempted to develop new anode materials [5]. Many anodes such as IrO_2,PbO_2, Pt, SnO_2, and boron-doped diamond have been extensively tested to select the suitable electrode that is stable and active towards organic electrochemical incineration [6–8]. Dopant SnO_2 and PbO_2 electrodes have good oxygen evolution overpotential. These electrodes are widely investigated as anode materials, and they perform well in electro-oxidation of organic pollutants. However, the main drawback of PbO_2electrode is the release of toxic ions in solutions, and the dopant SnO_2 electrode has limited work life [9]. IrO_2 electrode has low oxygen evolution overpotential, low current efficiency and high product selectivity [10], whereas platinum electrode show poor efficiency in electro-oxidation of organic pollutants [11,12]. Boron-doped diamond (BDD) film electrode represents an attractive anode material for electro-oxidation of organic pollutants especially refractory materials such as phenolic compounds, as well as different types of dyes and surfactants [13,14]. BDD electrodes have very wide potential window, high corrosion resistance, high oxygen evolution overpotential, inert surface and excellent electrochemical stability [15–18]. Although all BDD electrodes have superb electrochemical properties, they still have some drawbacks in mechanical properties for BDD film deposit on silicon and *Ti* substrate, and very high cost for BDD electrode film deposit on *W, Ta* and *Nb* substrates [9]. On the other hand, the surface area of BDD electrode is limited by the size of chemical vapor deposition (CVD) chamber. Diamond composite electrode with 40% of carbon black was used for the first time by King et al. [19], for the removal of microorganisms by indirect oxidation through in-situ formation of chlorine intermediate. There is no limitation on the dimension or shape of this electrode, and the cost of preparation is reasonable. Carbon black is used to increase the conductivity of semiconductor diamond electrode. To the best of our knowledge, data on the electrochemical behavior of carbon black diamond composite (CBD) electrodes are not reported in the open literature. In addition, these electrodes were not tested for the anodic oxidation of organic pollutants. As such, this

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research is the first of its kind to characterize the electrochemical behaviour and to apply the CBD electrodes for anodic oxidation of organic pollutants by direct oxidation process. Furthermore, this work reports the effect of carbon black (CB) percentage on the electrochemical properties of carbon black diamond composite (CBD) electrode such as potential window and oxygen evolution overpotential. Moreover, compare the oxidation potential of CBD electrodes with the oxidation potential of different anode materials. The electrochemical behavior of phenol on different CB percentage (i.e. 5%, 20% and 40%) in diamond electrodes was studied with cyclic voltammetry. Phenol was chosen as the model organic molecule for electro-degradation with CBD because it represents a basic unit in aromatic compounds [20] and it is well known to be difficult to degrade by anodic oxidation due to its tendency to cause fouling of the electrodes [21].

2. Experimental

2.1. Electrode preparation

Nanodiamond powder (98.3% purity, Sigma–Aldrich) with particle size of 3 to 10 nanometer was mixed carefully with CB nanoparticles (99% purity) with average particle size of 13 nanometer until the mixture became totally homogeneous. Four types of diamond carbon black composite electrodes were prepared depending on the percentage of CB (i.e. 5%, 10%, 20% and 40%). The homogeneous powders were mixed with liquid mixture consisted of 15% polytetrafluoroethylene suspension (60 wt%) in water (Sigma–Aldrich) as the binder and 85% of 1,3- propanediol (98% purity, Sigma–Aldrich). The liquid-to-powder ratio was 2:1 to ensure the mixture was sufficiently wet and able to mix for the preparation of the electrode paste. The electrodes paste was kneaded neatly, and then pressed in iron template to reduce the porosity of electrode. Then, the pressed paste was dried in an oven at 80 °C for 2 h, at 120 °C for 1 h, at 200 °C for 1 h [19] and at least 275 °C for 1 h to increase the hardness of the electrodes. Graphite bars were used as the current collectors by adhered to discs of 1.2 cm diameter of electrodes using silver conductive adhesive (Sigma–Aldrich) and then insulated by organic adhesive.

2.2. Electrochemical studies

Voltammetric experiments were carried out in one compartment of 100 mL glass cell at 25 °C. The solution composition was 0.5 M H_2SO_4 (97% Merck Pro Analysis), 0.5 M NaOH, and 0.5 M Na_2SO_4 (Merck GR for Analysis) with and without 0.5 g/L phenol (Merck GR for Analysis). Ultrapure water was used to prepare the solutions. The counter electrode was a platinum wire and Ag/AgCl was used as a reference electrode. Electrochemical measurements were performed by Autolab Metrohm potentiostat with NOVA 1.10 software, while ST-pHS3BW pH meter was used to check and adjust the pH of solutions. The working electrodes (CBD) were rinsed with distilled water, polished with sufficiently fine emery sheet, then rinsed with doubly distilled water prior to every experiment to make sure that the electrode surface is clean and free from any contamination.

2.3. Phenol degradation

For electrochemical degradation of phenol tests, electrochemical cell with 100 mL of 500 mg/L phenol solution and 0.5 M Na_2SO_4as supported electrolyte was used. The experiments were conducted with 50 mA/cm^2 constant applied current density, pH 3 and pH 6 and constant temperature of 25 °C. ISO-TECH programmable power supply IPS 3202 with constant current was used, whereas stainless steel cathode and C-MAG HS 7 magnetic stirrer was used for solution mixing.

2.4. Analysis method

The electrochemical degradation of phenol and its intermediates during electrolysis were examined by high performance liquid chromatography (HPLC) using an Agilent technology 1200 series. C18 column (4.6 mm × 150 mm × 5 μm) at 25 °C was used as the separation column for phenol and the electro-oxidation intermediate compounds, with the mobile phase acetonitrile/water (v/v) operate at 60/40 ratio and a flow rate 1 mL/min. The detection wavelength was set at 254 nm. The samples were filtered through a 0.25 μm membrane filter, and the injections volumes of HPLC were 5 μL. To identify the intermediate compound generated from phenol electro-degradation. The HPLC system was calibrated using standard analytical reagents prepared from common phenol degradation products namely benzoquinone, hydroquinone, catechol, malic acid, oxalic acid and fumaric acid. The electro-oxidation intermediate compounds were identified by comparing their retention times with those of the calibration standard run on the same HPLC under exactly the same conditions given above.

3. Results and discussion

3.1. Electrochemical characterization

Fig. 1 shows the background cyclic voltammetry curves for carbon black diamond (CBD) composite electrodes in 0.5 M H_2SO_4 . For 5CBD electrode, the background current was low and featureless between -0.75 and 2.6 V. Similarly 20CBD electrodes, the background current was also low and featureless between -0.35 to 2 V respectively. On the other hand, for 40CBD electrode, Fig. 1 illustrates that the background current was high and featureless between -0.4 to 1.35 V. It is obvious from Fig. 1 that the values of working potential windows for CBD electrodes are reduced by increasing carbon black percent. The working potential windows for 5CBD, 20CBD and 40CBD electrodes were 3.35, 2.4 and 1.75 V vs. Ag/AgCl respectively. The 5% CB diamond (5CBD) electrode working potential window was within the range of 3–4 V commonly reported for high quality polycrystalline boron-doped diamond (BDD) [21,22]. For diamond composite electrodes with 20% carbon black (20CBD), the potential window was less than 3 V and more than 2 V. It is typically observed for low quality polycrystalline boron-doped diamond electrode, which have a potential window close to that of carbonaceous electrodes [9,15]. The oxidation potential value of electrodes depends on the onset

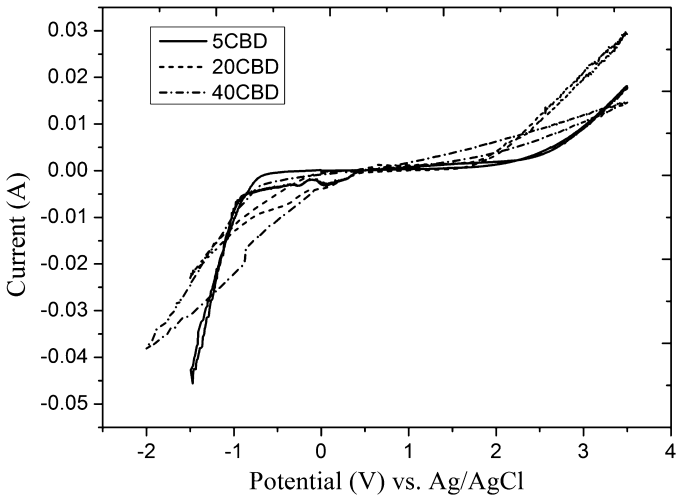

Fig. 1. Cyclic voltammetry for 5CBD, 20CBD and 40CBD electrodes in an aqueous solution of 0.5 M H_2SO_4. Scan rate 0.1 mV/s and 25 °C temperature.