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Applicability of boron-doped diamond electrode to the degradation of chloride-mediated and chloride-free wastewaters

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ABSTRACT

The electrochemical degradation of chloride-mediated and chloride-free dye wastewaters was investigated on a boron-doped diamond (BDD) electrode in comparison with that on a dimensionally stable anode (DSA), and the applicability of BDD electrode to the degradation of these two kinds of wastewaters was explored. In chloride-free wastewater, the electrochemical degradation efficiency of dye on BDD electrode was much higher than that on DSA, with a chemical oxygen demand (COD) removal of 100% and 26% for BDD and DSA, respectively. In chloride-mediated dye wastewater, COD removal was faster than that in chloride-free wastewater on both BDD and DSA electrodes with COD removal efficiencies higher than 95%, whereas the rate of COD removal on DSA was faster than that on BDD electrode. The investigation indicates that DSA is more suitable than BDD electrode in degradation of originally chloride contained dye wastewaters for the sake of energy and time saving. However, for chloride-free dye wastewaters, with the aim of environmental protection, BDD electrode is more appropriate to realize complete mineralization. At the same time, the secondary pollution can be avoided.

1. Introduction

Electrochemical oxidation techniques have been applied to the treatment of effluents from industrial plants. These techniques have various advantages, for instance, easy control, mild operation conditions, amenability to automation, environmental compatibility, high efficiency, and low cost [1–4]. As a high performance material with many excellent electrochemical features as wide potential, low background current, high oxygen evolution potential, and stable dimension and mechanical properties, boron-doped diamond (BDD) electrode has been arousing a lot of research interests, and is extensively used to electrochemical degradation of organic pollutants. Many of the biorefractory pollutants were decontaminated completely using BDD electrode [5–8]. The electrochemical oxidations for naphthalenesulfonates [9], sodium dodecylbenzenesulfonate, and hexadecyltrimethyl ammonium chloride [10] were studied, and these surfactants were mineralized completely. Alizarin red, eriochrome black T [11], indigo carmine [6], and other dye wastewaters [12,13] were degraded by BDD electrode, and the chemical oxygen demand (COD) removal efficiency was higher than 95%. Highly toxic herbicide or pesticide, such as 4-chloro-2-methylphenoxyacetic acid, 2-(4-chlorophenoxy)-2-methylpropionic acid, 2-(4-chloro-2-methylphenoxy)propionic acid [14], diuron, and 3,4-dichloroaniline [5], were also mineralized completely by BDD electrode.

Electrochemical methods for wastewater treatment mainly involve the direct and indirect electrochemical oxidation. The direct electrolysis is a process that organic pollutants are directly oxidized on the anode electrochemically with no intermediates. By indirect electrolysis, organic pollutants can be degraded by generating in situ strong oxidative intermediates that convert these pollutants into less hazardous products. The main oxidizing agent is active chlorine compounds, such as gaseous chlorine, hypochlorous acid, and hypochlorite ions, which are anodically produced from original chlorides present in the wastewater [15]. The active chlorine compounds can electrochemically oxidize organic molecules quickly. This process is irreversible due to the intense oxidative activity of active chlorine compounds. It is obvious that a much faster COD removal will be obtained by indirect oxidation owing to strong oxidative chlorine compounds formed during electrolysis. However, gaseous chlorine, hypochlorous acid, and hypochlorite ions produced during the indirect electrolysis are highly toxic and caustic. Moreover, gaseous chlorine can be easily interacted with organic molecules and form carcinogenic, mutagenic, and teratogenic halogen compounds. Therefore, we hope that pollutants can be mineralized during the direct oxidations in solutions without the formation of active chlorine compounds to avoid this secondary pollution.

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As far as is known, the efficiency of electrochemical oxidation is pertinent to electrode materials and supporting medium, and some studies have been performed in wastewaters containing low concentration of organic pollutants [15,16]. The experimental results have indicated that the efficiency of electrochemical oxidation in chloride-mediated wastewaters is higher than that in chloride-free wastewaters for most of electrodes. However, whether BDD electrode can present its electrochemical excellence over other electrode materials under various conditions is rarely reported.

The color and low light transmissivity of high concentration dye wastewater restrain a possible application of photocatalytic decomposition. Therefore, in this work, a study on the electrochemical oxidation behavior and degradation process of a synthetic solution containing high concentration methylene blue (MB), a dye widely used in many fields, in supporting electrolytes with and without chloride ions will be conducted on BDD electrode. And the comparative research of electrochemical degradation efficiency on BDD electrode and a dimensionally stable anode (DSA) will be performed to assess the applicability of BDD to degrade a dye in chloride containing and chloride-free model wastewater.

2. Experimental

2.1. Chemicals and materials

All chemicals used in the experiments were of analytical pure grade and used without further purification. The concentration of MB in wastewater for these experiments was 1000 mg/L with a corresponding COD value of 1371 mg/L. 0.05 mol/L Na_2SO_4 solution was used as supporting electrolyte, and NaOH or H_2SO_4 in proper amounts was used to get suitable pH value.

BDD electrode was deposited on Si wafers by microwave plasma chemical vapor deposition (MWCVD) [17]. DSA electrodes were made of a titanium base covered by metal oxides (iridium and ruthenium oxides in our case).

2.2. Electrolytic system

Galvanostatic electrolyses with imposed current density of 20 mA cm^{-2} were performed in an undivided three-electrode cell. 50 ml solution was degraded in each experiment and stirred at constant temperature (25 °C). The anode was a square plate of BDD electrode or DSA with effective surface area of 5 cm^2, whereas the cathode was a Ti square plate of 5 cm^2, and the gap between electrodes was 10 mm. A saturated calomel electrode (SCE) was used as reference.

2.3. Analytical procedure

The electrochemical behavior of wastewater was studied using CHI660A electrochemical working station (CHI, USA) by linear sweep voltammetry (LSV) using a conventional three-electrode cell at 25 °C. The working electrode was a BDD electrode or DSA, the counter electrode was a Pt wire, and the reference electrode was SCE. LSV was performed with unstirred solutions at scan rates (v) of 100 mV s^{-1}. All potentials are referred vs. SCE unless otherwise stated.

The UV–vis spectra of dye were recorded in 200–800 nm range using a UV–vis spectrophotometer (Agilent 8453) with a spectrometric quartz cell (1 cm path length).

COD of the same solutions was monitored by dichromate titrimetric method as described in standard methods.

3. Results and discussion

3.1. Electrochemical oxidation behavior of dye wastewater on BDD electrode

The electrochemical oxidation behavior of MB during the electrochemical degradation on BDD was studied; and the results obtained in electrolytes with and without Cl^- are shown in Figs. 1 and 2, respectively. Three oxidation peaks at 0, +0.25, and +1.46 V are observed in both Cl^--mediated and Cl^--free wastewaters before electrochemical degradation, which indicates a multistep oxidation process of MB on BDD. Thus, MB can be electrochemically degraded on BDD under both conditions. The dependence of oxidation current on degradation time at peak potential is shown in Figs. 1B and 2B. It can be observed that the oxidation peak at 0 and +0.25 V decreases quickly with the electrolysis time, whereas the oxidation peak at +1.46 V decreases more slowly. The largest difference between the direct electrolysis and indirect electrolysis is proved by the different electrochemical behavior of oxidation peak at +0.85 V. No oxidation peaks is observed at +0.85 V before degradation. There is still no oxidation peak at +0.85 V during direct electrolysis. Although the current at +0.85 V increases at first and then decreases, it maintains at low value during electrolysis. However, the oxidation peak is observed at +0.85 V and reaches the highest value in 30 min during indirect electrolysis. As the electrolysis time increases, the peak current decreases gradually. It may be assumed that some electroactive chlorine compound is formed during the indirect electrolysis. Further, the concentration of chloride ions in wastewater solutions decreased gradually, and then the

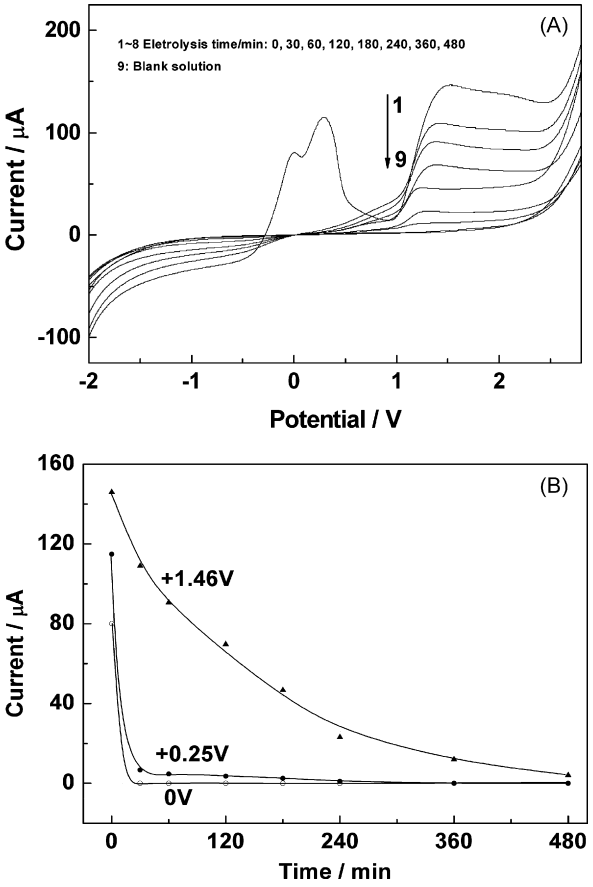

Fig. 1. (A) Linear sweep voltammetrogram of MB in electrolytes without chloride on BDD during electrolysis; (B) dependence of oxidation current at 0, +0.25, and +1.46 V on electrolysis time.