Research Article

Comparison of BDD and SnO₂ Electrodes for Carbendazim Electro-oxidation

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Abstract
The anodic oxidation is a promising process for degrading toxic and organic pollutants present in wastewater treatment. Suitable selection of electrodes is the key to reach effective and economic operation. In this study, two types of electrodes, BDD and SnO₂, which is generally believed that the BDD electrode be superior to the usual electrodes, were compared under the same conditions. It was found that BDD electrode could mineralize our pesticide effectively. But the SnO₂ electrode could only mineralize less than BDD. When oxidizing more refractory pesticide, it demonstrated very poor activity. The straight experimental comparison in the present study indicates that the BDD electrode is much better than the SnO₂ electrode for pesticide oxidation.

Keywords: Pesticide, electrooxidation, BDD, SnO₂, carbendazim

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Introduction
In the recent past two decades, anodic oxidation has been widely investigated for wastewater treatment. Its high oxidation efficiency, fast reaction rate, and easy operation make it a very attractive alternative to the conventional processes for degrading toxic organic pollutants. Specifically, the electro-oxidation process has been shown to be attractive for the mineralization of organic pollutants from wastewater. Concentrated and refractory organics could be mineralized on the electrode during anodic oxidation process. It is well known that proper selection of electrodes is one of great importance for effective and economical operation. Good electrodes should be not only effective for pollutant degradation, but also stable electrochemically. Up to date, numerous types of electrodes including Pt [1], graphite[2,3], PbO₂ [4-8], SnO₂ [7, 9-11], IrO₂ [11-13], Pt–Ir [14], RuO₂ [15], glassy carbon [16], fiber carbon [17], MnO₂ [18, 19], TiO₂ [20, 21], and boron-doped diamond (BDD) have been investigated. SnO₂ electrodes are generally believed to be superior to Pt, graphite, PbO₂, and many other common electrodes. Pure SnO₂ is an n-type semiconductor with a band gap of about 3.5 eV. BDD, has received growing attention for pollutant oxidation. Undoped synthetic diamond is an insulator with a resistivity of >106 Wm and a band gap energy of 5.5 eV [22]. However, the conductivity of diamond can be significantly improved by doping with boron. Usage of BDD electrodes for pollutant removal was first reported by Tenne and co-workers in 1993 [23]. They investigated the reduction of nitrate to ammonia on a BDD cathode. Carey and coworkers [24] patented the use of BDD electrodes as anodes for organic pollutant oxidation in 1995. Since then, anodic oxidation of various model pollutants such as phenol [25, 26], cyanide [27], carboxylic acids [28], 3-methylpyridine [29], 2-naphthol [37], 4-chlorophenol [30], 4-chlorophenoxyacetic [31], benzoic acid [32], polyacrylates [33], and dyes [34] on BDD electrodes was investigated.
Experimental

Chemicals

Carbendazim is fungicide that is used in a number of crops to help control the growth of unwanted fungus and mold. If left untreated, mold, fungus, pests and insects on crops can damage the safety and quality of our food supply. Carbendazim formulation is commercially available in the LASKOR 50 WG (50% Carbendazim) Fig.1.

Figure 1 Chemical structure of carbendazim

Electrolytic system

Electrochemical measurements were performed using a computer controlled by potentiostat/ Galvanostat model PGZ 100 associated to "Volta-Master 4" software.

A conventional three-electrode cell (100 cm³) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anodes were a square plate of BDD and SnO₂ electrodes with effective surface area of 1 cm² for each one, whereas the cathode was a platinum electrode, and the gap between electrodes was 0.5 cm. A saturated calomel electrode was used as a reference. Galvanostatic electrolysis was carried out with a volume of 75 cm³ aqueous solution of 30 mgL⁻¹ de carbendazim. The range of applied current was 40–80 mAcm⁻² and samples were taken, at predetermined intervals during the experiment, and submitted for analysis. All tests were performed at (25 ± 3)°C in magnetically stirred and aerated solutions. In all cases, sodium chloride was added to the electrolytic cell, at different concentrations.

The chemical oxygen demand (COD) measurement during the processing permitted the evaluation of the kinetic of organic matter decay and the mineralization efficiency. COD was determined by dichromate method. The appropriate amount of sample was introduced into prepared digestion solution (0-1500mg O₂.L⁻¹) containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 2h at 150°C in COD reactor (WTW CR 3200 thermoreaktor, Germany). COD concentration was measured calorimetrically using AFNOR Method.

Results and Discussion

Cyclic voltammetric behavior

It was observed that the voltammogram shape changed gradually for the SnO₂ electrode during scanning. The situation for the BDD electrode was different. A relatively large voltammetric current was detected initially. The voltammetric current decreased quickly, however. This indicates that the BDD electrode may have higher electrochemical stability. Fig.2 and Fig.3 shows the voltammograms obtained on the BDD and SnO₂ electrodes after reaching steady state. The SnO₂ has an onset potential of 1.12 V vs SCE for O₂ evolution. In contrast, the onset potential for O₂ evolution on the BDD electrode is 1.735 V vs SCE, 0.608 V higher than that obtained on the SnO₂.
electrode. It should be noted that high onset potential for O₂ evolution is desired because O₂ evolution is a side reaction in the process of anodic oxidation of pollutants. The much higher onset potential for O₂ evolution suggests that the BDD electrode may have much higher current efficiency than the SnO₂ electrode for pollutant oxidation.

![Graph showing cyclic voltammograms](image1)

**Figure 2** Cyclic voltammograms obtained on SnO₂ electrode after reaching steady state.

![Graph showing cyclic voltammograms](image2)

**Figure 3** Cyclic voltammograms obtained on BDD electrode after reaching steady state.

**Activity**

In order to compare the activity between BDD and SnO₂ electrodes, oxidation of carbendazim, which among one of toxic organic pollutants present in agricultural effluents, was investigated first. Fig.4 shows the COD variations with charge. It was found that both electrodes could mineralize carbendazim. But the bdd electrode was more effective than the SnO₂ electrode. At a charge of 160C the BDD electrode reduced COD from initial 920 mg.L⁻¹ to 345 mgL⁻¹.
In contrast, the SnO₂ electrode could only reduce COD to about 523 mg L⁻¹ at the same charge and during two hours. In attempt to lower COD to a level of 345 mg L⁻¹, a twofold charge was required.

Figure 4 Oxidation of 30ppm carbendazim, reaction temperature 25°C, NaCl 0.1 g/L.

Effect of NaCl concentration

It could observed from Figure 5 and Figure 6 that, when the concentration of NaCl is over than 0.1 g/L (0.2; 0.3; 0.4). The treatment had little effects. The NaCl concentration was more than enough to oxidize the pollutants in the water. In other hand we observed that the degradation of BDD electrode is more higher than SnO₂, as a results we found that with BDD we have obtained 62.5% as COD removal that equal to 345 mg/L of COD (mg/L), higher than 43.15% and 523 mg/L after three hour of degradation [35-37].

Figure 5 Influence of NaCl concentration on oxidation by BDD
Figure 6 Influence of NaCl concentration on oxidation by SnO2

Effect of current density

Carbendazim with different values of current density, (between 20mA to 80mA). And two electrodes the latter BDD and the former SnO2. The reaction lasted 3 hours after obtaining all samples for measuring COD.

The influence of current density on treatment with two different electrodes is shown in Figure 7 and Figure 8 [35-39].

Figure 7 Influence of current density on oxidation by BDD
It can be seen that current density has a significant effect on the treatment of wastewater using BDD electrode more better than SnO2, whose we have obtained 62.5% COD removal against 43.15% for SnO2.

**Effect of initial concentration of carbendazim**

**Figure 9** and **Figure 10** shown the results for carbenazim degradation on two electrodes in multi initial carbendazim concentration resulted in a relatively lower COD removal.
However, the decrease trend was different on two electrodes. The COD removal decrease from 54.07% to 18.29%. However on the BDD electrode, such a decrease was not so evident (within 10%). This fact supported that the electrochemical degradation on BDD performed better in relative wide concentration ranges, which made it much more promising for application. It should be noted that though the COD removal was decreased at a higher initial concentration, the COD degradation was increased [37-38]. In reason to confirm the quality of BDD in degrading carbendazim that was confirmed by using UV spectra shown in fig.6 as taking blanc as reference (absence of degradation) and two samples were oxidizing both electrodes, as a results BDD is better than SnO$_2$ in degradation of carbendazim.

**Conclusion**

The performances of BDD and SnO$_2$ were compared under the same conditions. Experimental results indicate that the BDD is a much better electrode than the SnO$_2$ is terms of both electrochemical activities and operating conditions. The COD removal for BDD electrode is over 20% for all the experiments done while that for SnO$_2$ is always significantly below 20%. The BDD can mineralize carbendazim while SnO$_2$ works for carbendazim but not like BDD.

**References**


