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Study of Electrochemical Oxidation and Quantification of the Pesticide Pirimicarb Using a Boron-Doped Diamond Electrode

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ABSTRACT

An electrochemical study of the carbamate pesticide pirimicarb (PMC), which acts on the central nervous system, was performed using a boron-doped diamond working electrode. Cyclic, differential pulse, and square-wave voltammetry experiments across a wide pH range (2.0 to 8.0) showed three irreversible oxidation processes in the voltammetric behavior of PMC. The two first processes were pH-dependent, while the third was not. The three oxidation process were independent of each other, and each involved the transfer of one electron. A reaction proposal for the electrochemical oxidation of PMC is shown, and it is supported by mass spectrometry experiments. After this, an analytical method for PMC quantification in water samples by differential pulse (DP) voltammetry is proposed. The optimal DP voltammetric parameters (step potential, amplitude potential, and scan rate) were optimized using experimental design, and an analytical curve was obtained from 2.0 to 219 μmol L^{-1} with an estimated detection limit of 1.24 μmol L^{-1}. The accuracy of the proposed method was evaluated by the addition and recovery method, with recoveries ranging from 88.6 to 96.3%. Some highlights of the proposed analytical method are its simplicity, reliability, and portability.

1. INTRODUCTION

Although pesticides are used to enhance food quality by eliminating or preventing pest infestation in plant cultures [1], they can be harmful to the health of humans and animals. In addition, their use is increasing as a consequence of population growth, which increases the demand for food production [2]. Currently, the pesticide industry is one of the world's largest, with expenditures reaching tens of billions of dollars annually [3]. Carbamate pesticides are one of the major classes of pesticides used around the world, and are largely used because of their broad spectrum of biological activity [4].

Pirimicarb ([2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl] N,N-dimethylcarbamate; PMC) is a carbamate pesticide classified as "likely to be carcinogenic to humans" [5,6]. PMC shows a reasonable water solubility about 2,700 mg L^{-1} [7]. The Brazilian laws prescribe that the maximum residual level (MRL) of PMC varies from 0.05 to 1 mg kg^{-1}, depending on the type of crop [8]. At USA, according to the Environmental Protection Agency, there are no products containing PMC [9] and in Europe the use of PMC is authorized in several countries [10]. The exposure to carbamates pesticides is associated with leukemia [11]. The biological mechanism of carbamate pesticides is associated with the inhibition of the acetylcholinesterase enzyme (AChE), which is responsible for the breakdown of excessive amounts of the neurotransmitter acetylcholine. Excess acetylcholine is called cholinergic crisis, and will result in an interruption of neural signals [12] and various health problems [13,14]. Thus, studies focusing on understanding the mechanism of action of this pesticide are important. Electrochemical techniques such as voltammetry are powerful tools that can provide insights into the mechanisms of action of a range of compounds [15]. In addition, the development of sensitive, reliable, and accurate analytical methods for monitoring PMC in different matrices should be pursued.

The most common method of detecting and quantifying PMC is the use of an extraction method coupled with high performance

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liquid chromatography with ultraviolet detection (HPLC-UV) [16–24]. Liquid chromatography with mass spectrometry (LC-MS) [25] and tandem mass spectrometry detectors (LC-MS/MS) [26,27], ultra-high performance liquid chromatography with tandem mass spectrometry detectors (UPLC-MS/MS) [28], gas chromatography with mass spectrometry (GC-MS) [29,30], tandem mass spectrometry (GC-MS/MS) [31], nitrogen-phosphorous (GC-NPD) [17,30,32], and electron capture (GC-ECD) [32] detectors are also used. Methods based on capillary electrophoresis with UV [33] or mass spectrometry detection [34], electrochemiluminescence [35], voltammetric biosensors [4,36], and polarography [37] can also be found in the literature.

Most of the previously mentioned methods are very reliable; however, they show some disadvantages based on the use of expensive instrumentation or biological materials that require specialized sensor storage or experimental conditions. In addition, they are not easily portable, and some of them use hazardous materials such as mercury, or are laborious and require well-trained staff, making their implementation in routine and field analyses difficult. However, electroanalytical techniques offer some advantages including easy portability, suitable sensitivity, and relatively inexpensive instrumentation [14,38], as the sensor material plays an important role in terms of both analytical parameters and price. Thus, the use of unmodified electrodes, or those requiring only experimentally simple modifications, can reduce the cost of the sensor, making it more attractive for implementation in routine or in-field analysis.

It is possible to find some electrochemical studies of PMC in the literature. Pingarrón and coworkers [39] studied the anodic behavior of PMC using a glassy carbon electrode in a aqueous (Britton-Robinson buffer) and organic media. Based on the experiments performed, the authors observed two oxidation processes in aqueous media, while in acetonitrile it was possible to observe three oxidation processes by differential pulse voltammetry. After studying the electrochemical properties of PMC, the authors reported an analytical method for detecting PMC in soil samples using differential pulse voltammetry in acetonitrile medium with an estimated detection limit of 6.1×10^{-7} mol L^{-1}. In an earlier study, Batley and Afgan [40] examined a range of pesticides in aqueous media, including PMC. The study was performed by cyclic voltammetry using a glassy carbon electrode, and the authors observed an oxidation process at +1.15 V vs. a saturated calomel reference electrode (SCE). The authors also commented that the voltammetric signal appeared as a shoulder in the region of the oxygen evolution wave, and that the resolution of the signal varied with the electrode age. This was considered a drawback to the use of this electroanalytical method to measure PMC.

A problem associated with carbamate pesticides is related to the potential required to oxidize them. This class of pesticide requires a very large oxidation potential, which is not always easy to achieve using conventional electrodes materials such as glassy carbon, platinum, or gold. For this reason, most of the electrochemical methods found in the literature make use of an alkaline derivatization process [38,41,42] when reporting analytical methods. In addition, oxidation products may adsorb onto the electrode surface, increasing the difficulty of monitoring such compounds. Boron-doped diamond (BDD) electrodes have emerged as a promising material for use in voltammetric analysis due to its beneficial characteristics, which include large anodic and cathodic potential ranges (>±2 V), low background currents, and minimal adsorption. The electrochemical features of the BDD electrodes are directly linked to the boron doping level necessary to become the material conductive, but in higher doping levels the BDD electrode exhibits high amount of sp^2 sites enhanced the adsorption of organic materials and the background current, as well as, narrowing the potential window [43–46]. Thus, BDD electrodes are an excellent alternative for overcoming the limitations of more conventional electrodes [41]. In addition, BDD electrodes can be considered eco-friendly as they can be used to replace mercury as a working electrode in numerous analyses.

This work presents an electrochemical study of the carbamate pesticide PMC using a boron-doped diamond electrode in cyclic voltammetry, differential pulse voltammetry, and square wave voltammetry, as well as mass spectrometry. Additionally, a sensitive and accurate electroanalytical method for quantifying the pesticide in natural water by differential pulse voltammetry is proposed.

2. EXPERIMENTAL

2.1. Reagents and solutions

All chemicals were used as received. Pirimicarb (98.7%) was acquired from Sigma-Aldrich® (St. Louis, MO, USA, catalogue number 45627). All others chemicals were of analytical grade and were used without any further purification.

Aqueous solutions were prepared using deionized water obtained from a water purification system (Direct-Q® 5 Ultrapure Water Systems, Millipore, MA, USA) with a resistivity >18.1 MΩ cm. A PMC stock solution (10 mmol L^{-1}) in acetonitrile (Merck®, Darmstadt, Germany) was prepared for cyclic voltammetry (CV), whereas an 1.00 mmol L^{-1} solution in a mixture of acetonitrile (20% v/v) and phosphate buffer solution (pH 7, 80% v/v) was prepared for the differential pulse (DP) voltammetry and square wave (SW) voltammetry experiments. A 0.5 mol L^{-1} sulfuric acid solution was used for cathodic and anodic pretreatment of the boron-doped diamond electrode surface. Table S1 (Supplementary Information) lists the compositions and pH values of the buffer solutions used as supporting electrolytes for the pH study. The ionic strength (I) of all buffers was controlled to be at least 0.1 mol L^{-1} using sodium sulfate.

Tetrabutylammonium tetrafluoroborate (TBATFB) acquired from Sigma-Aldrich® and anhydrous acetonitrile were used to prepare the supporting electrolyte for the voltammetric experiments in organic media.

2.2. Electrochemical instrumentation and measurements

The pH values of the buffer solutions were measured using a Metrohm pH meter (Herisau, Switzerland, model 827 pH lab) coupled to a glass electrode (model Unitrode PT1000).

The electrochemical measurements were carried out using a potentiostat/galvanostat Autolab PGSTAT128N (Eco Chemie, Utrecht, The Netherlands) controlled by a laptop running NOVA 1.11.2. A standard three-electrode configuration was used in the voltammetric measurements. A BDD film with a doping level of approximately 8000 ppm chemical vapor deposited (CVD) on a polycrystalline silicon wafer (8×8 mm^2) was obtained from NeoCoat SA (La Chauxde-Fonds, Switzerland). The BDD film was used as the working electrode coupled to an electrochemical cell, as reported in previous work [47]. The counter and reference electrodes were a platinum coiled wire and a home-made Ag|AgCl| KCl (3 mol L^{-1}) electrode [48], respectively.

2.2.1. CV experiments

Exploratory CV experiments were carried out at different pH values (2, 3, 4, 5, 7, and 8). The BDD electrode was cathodically pretreated before each measurement in 0.5 mol L^{-1} sulfuric acid solution by applying potentials of +3 V for 5 s and −3 V for 60 s to ensure consistent conditions at the electrode surface. Exploratory CV experiments were carried out from −0.5 to 2 V at a scan rate (v)