



## Electrochemical degradation of the insecticide methyl parathion using a boron-doped diamond film anode



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### ABSTRACT

Methyl parathion is one of the most toxic of the organophosphate insecticides. While this agent continues to be used, natural waters in agricultural areas are likely to contain significant amounts of the biocide, representing a threat to beneficial insects, freshwater organisms, birds and mammals. The electrochemical oxidation of methyl parathion in acidic medium has been studied using a boron-doped diamond (BDD)/Ti anode under galvanostatic current control. Chronoamperometry showed that significant oxidation of reference standard methyl parathion commenced at 1.8 V vs Ag/AgCl, while spectrophotometric studies revealed that the absorbance of a commercial formulation of the insecticide decayed according to time in electrolysis. Electrochemical degradation experiments were performed in a laboratory-constructed polypropylene cell in which solutions containing methyl parathion (equivalent to 60 mg L<sup>-1</sup>) were subjected to electrolytic treatment at different current densities (5, 10, 25, 50 and 100 mA cm<sup>-2</sup>). High performance liquid chromatographic analysis demonstrated that 81.2% of the insecticide was removed in 180 min at an applied current density of 100 mA cm<sup>-2</sup>, and a compound, identified from its UV spectrum as 4-nitrophenol, was formed either as an intermediate or as a byproduct. Under these conditions, mineralization efficiency (determined by total organic carbon analysis) was 67.6%, and the toxicity of the original electrolyte against the bioluminescent bacterium *Vibrio fischeri* was reduced considerably by the electrochemical treatment. It is concluded that electrooxidation using BDD/Ti electrodes represents an appropriate method for the removal of methyl parathion from contaminated waters.

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### 1. Introduction

Brazilian agriculture has become increasingly dependent in recent years on the use of chemical fertilizers and pesticides to maintain and augment yields. The key crops of soybean, corn, cotton and sugarcane presently account for some 80% of the total industrial production of pesticides in the country, and Brazil now ranks as one of the largest consumers of these biocides in the world. The intense use of toxic agrochemicals has led to increased contamination of ground and surface water, and escalated the level of concern about the effects of this type of environmental pollution on public health [1].

Methyl parathion [O,O-dimethyl O-(4-nitrophenyl) phosphorothioate] is one of the most toxic of the organophosphate biocides, and acts as a non-systemic insecticide and acaricide through tissue contact and via the gastrointestinal tract. The broad-spectrum insecticide was authorized for use in the control of pests on cotton,

garlic, rice, potatoes, onions, beans, corn, soybean and wheat cultivations [2]. Following application, most of the insecticide generally remains in the immediate locality, although some may be transported away by the action of wind and rain. Methyl parathion persists in the environment for a few days up to several months depending on the local conditions. In water and air, however, the insecticide may be broken down by the action of ultraviolet radiation to form the more toxic methyl paraoxon [3].

Methyl parathion is classified as highly toxic to beneficial insects as well as to freshwater, estuarine and marine organisms. The insecticide poses significant acute and chronic risks to birds, while mammals may be adversely affected by the toxin through oral or dermal exposure and by inhalation [4]. In humans, the biocide is considered an endocrine disruptor since studies have shown that it induces hyperglycemia and hypoinsulinemia in the murine model, affects the development of the embryo and fetus in pregnancy [5], and increases the activity of aromatase, an enzyme responsible for the conversion of androgens into estrogens [6].

In consideration of its harmful effects on human health, methyl parathion has been banned in the European Union and its use is restricted in the USA. Although the insecticide remains available on

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the Brazilian market, the National Health Surveillance Agency (ANVISA) has recently entered into public consultation concerning reclassification of the agent with a recommendation to ban the sale of the product [7].

While the pesticide continues to be used, natural waters in agricultural areas are likely to contain significant amounts of the toxin. In the USA, for example, concentrations of methyl parathion of up to  $0.46 \mu\text{g L}^{-1}$  have been reported, with the highest values being recorded during the summer months [2]. Additionally, the removal of pesticides from aqueous environments remains especially challenging since the technologies associated with conventional treatments are unable to eliminate such contaminants efficiently.

Various approaches are available for the removal of organic pollutants from wastewater, and these include incineration, oxidation with strong oxidants and the application of biological methods. Recent interest has focused on the use of advanced oxidation processes (AOPs) based on the production of hydroxyl radicals that successively attack organic compounds. In this context, electrochemical AOPs have received considerable attention by virtue of their energy efficiency, versatility and amenability to automation. A particular advantage of electrochemical AOP is that mineralization of the organic pollutants consumes only electrical energy and no exogenous chemical reagents are employed [8].

The anode plays a key role in an electrochemical AOP and the careful choice of anodic material is fundamental to the success of the process. The anode should present satisfactory efficiency, cost-effectiveness and stability even under extreme conditions of, for example, pH and time of electrolysis. Electrodes produced using various materials, including Pt,  $\text{PbO}_2$  and mixed metal oxides (dimensionally stable anode; DSA), have been tested for application in wastewater treatment with varying degrees of success [9,10]. Particularly attractive results regarding the degradation of diverse organic pollutants have been obtained with electrodes comprising boron-doped diamond (BDD) films [11–18]. In comparison with other electrode materials, conductive diamond appears to offer a number of advantages, including a high overpotential for water electrolysis and enhanced stability [19]. In particular, the hydroxyl radicals that appear to be directly involved in oxidation mechanisms occurring at BDD surfaces are produced with high efficiency within a large potential window [20].

BDD electrodes appear to be particularly valuable in the treatment of effluents containing pesticides. Thus, Errami et al. [21] reported efficient electrochemical oxidation of the insecticide buprofezin pesticide using BDD anodes. In this example, 98% of the chemical oxygen demand (COD) could be removed from solution when the experimental conditions (i.e. electrolyte, pH, concentration of buprofezin, and time of experiment) were optimal.

The aim of the present study was to investigate the electrochemical degradation of methyl parathion in acidic electrolyte using an electrode comprising BDD film deposited on a Ti plate. The influence of applied current density on the removal of total organic carbon (TOC) and on the rates of reduction of concentration and of toxicity of a commercial formulation of methyl parathion was determined.

## 2. Experimental

### 2.1. Preparation of BDD electrodes

A film of BDD was grown on a Ti plate ( $25 \times 25 \times 0.7 \text{ mm}$ ) using the hot filament-chemical vapor dispersion (CVD) technique. A mixture of  $\text{H}_2$  and  $\text{CH}_4$  with constant composition (99:1, v/v) was supplied through the main gas line, while doping was controlled by an additional flow of  $\text{H}_2$  that passed through a bubbler containing a solution of  $\text{B}_2\text{O}_3$  in  $\text{CH}_3\text{OH}$  with a B/C ratio of 15,000 ppm. The

flux of  $\text{H}_2$  carrying the doping agent through the additional line was controlled by means of a rotameter, and the temperature and pressure within the reactor were maintained at 923 K and 5.3 kPa, respectively.

The composition, morphology and electrochemical characteristics of the electrodes produced using this method have been previously assessed by our group through detailed studies involving Raman spectroscopy, scanning electron microscopy and cyclic voltammetry. It has been established that the diamond films cover the entire surface of the Ti plates homogeneously, and that the boron content within the films can attain  $7.09 \times 10^{20} \text{ atoms cm}^{-3}$  according to Mott-Schottky Plot measurements. Moreover, the potential window of the BDD/Ti electrode was determined to be ca. 2.5 V vs Ag/AgCl with 3.0 M KCl in  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at a scan rate of  $30 \text{ mV s}^{-1}$  [22].

### 2.2. Electrochemical behavior of methyl parathion

Chronoamperometric and cyclic voltammetric analyses of analytical standard grade methyl parathion (99.9% pure; Sigma-Aldrich, St. Louis, MO, USA; product # PS407 Supelco®) in  $0.1 \text{ M H}_2\text{SO}_4$  (analytical grade reagent; Synth, Indaiatuba, SP, Brazil) were conducted at room temperature in a conventional three-electrode cell of volume 0.35 L. The working electrode was a BDD/Ti plate (area  $4.15 \text{ cm}^2$ ), the counter electrode was a Pt wire and the reference electrode was a commercial Ag/AgCl electrode (Analyser Co. São Paulo, SP, Brazil) with 3.0 M KCl solution. Electrochemical measurements were performed using a Metrohm Autolab (Utrecht, The Netherlands) model PGSTAT-302 potentiostat/galvanostat coupled with a model BSTR-10A current booster and controlled by GPES software. Chronoamperograms were acquired with continuously stirred solutions, while cyclic voltammograms were obtained with unstirred solutions at a scan rate of  $30 \text{ mV s}^{-1}$ . Prior to each experiment, the surface of the BDD/Ti electrode was cleaned with isopropyl alcohol in an ultrasonic bath for 5 min.

### 2.3. Electrochemical degradation of methyl parathion

The commercial insecticide Folisuper 600 BR (Agripec Química e Farmacêutica S/A, Maracanaú, CE, Brazil), containing  $600 \text{ g L}^{-1}$  of the active constituent methyl parathion, was employed in the degradation experiments. The electrolytic solution contained  $100 \text{ mg L}^{-1}$  of the commercial insecticide (equivalent to  $60 \text{ mg L}^{-1}$  of methyl parathion) in  $0.1 \text{ M H}_2\text{SO}_4$  (analytical grade reagent; Synth) as supporting electrolyte, and presented a TOC value of  $38 \text{ mg L}^{-1}$ . All electrolyte solutions were prepared with purified water obtained using a Millipore Milli-Q water purification system ( $18.2 \text{ M}\Omega \text{ cm}$ ; TOC value  $0.0095 \text{ mg L}^{-1}$ ).

Electrochemical degradations were performed in a laboratory-constructed polypropylene cell maintained at  $25^\circ\text{C}$  [13]. The working BDD/Ti electrode was positioned at the bottom of the cell, while the counter (platinum spiral) and reference (Ag/AgCl) electrodes were located at the top. Anodic oxidation of the substrate solution was performed under galvanostatic conditions by applying current densities of 5, 10, 25, 50 and  $100 \text{ mA cm}^{-2}$  (values determined from chronoamperometry studies). Prior to each experiment, the surface of the BDD/Ti electrode was cleaned with isopropyl alcohol in an ultrasonic bath for 5 min.

Electrochemical degradation was also performed using a solution containing  $60 \text{ mg L}^{-1}$  of analytical standard grade methyl parathion (Supelco, Bellefonte, PA, USA) in  $0.1 \text{ M H}_2\text{SO}_4$  (analytical grade reagent) with an applied current density of  $50 \text{ mA cm}^{-2}$  in order to identify possible intermediates formed during the reaction.

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