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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^{-1}) were subjected to electrolytic treatment at different current densities (5, 10, 25, 50 and 100 mA cm^{-2}). 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^{-2}, 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 BBD/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 $\mu g\ L^{-1}$ 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, 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 × 25 × 0.7 mm) using the hot filament-chemical vapor dispersion (CVD) technique. A mixture of H_2 and 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 H_2 that passed through a bubbler containing a solution of B_2O_3 in CH_3OH with a B/C ratio of 15,000 ppm. The flux of 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 homogenously, and that the boron content within the films can attain 7.09×10^{20} atmos 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 mol L^{-1} H_2SO_4 at a scan rate of 30 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 M H_2SO_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 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 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 g L^{-1} of the active constituent methyl parathion, was employed in the degradation experiments. The electrolytic solution contained 100 mg L^{-1} of the commercial insecticide (equivalent to 60 mg L^{-1} of methyl parathion) in 0.1 M H_2SO_4 (analytical grade reagent; Synth) as supporting electrolyte, and presented a TOC value of 38 mg L^{-1}. All electrolyte solutions were prepared with purified water obtained using a Millipore Milli-Q water purification system (18.2 MΩ cm; TOC value 0.0095 mg L^{-1}).

Electrochemical degradations were performed in a laboratory-constructed polypropylene cell maintained at 25 °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 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 mg L^{-1} of analytical standard grade methyl parathion (Supelco, Bellfonte, PA, USA) in 0.1 M H_2SO_4 (analytical grade reagent) with an applied current density of 50 mA cm^{-2} in order to identify possible intermediates formed during the reaction.

2.4. Analytical procedures

The UV–VIS spectra of samples of electrolyte obtained during the electrochemical degradations were measured in the range 200–800 nm on a Varian (Agilent Technologies, Santa Clara, CA, USA) Cary 50 spectrophotometer using a quartz cuvette with an optical path of 1 cm. Concentrations of analytes were estimated from absorbencies recorded at 277 nm.

The amounts of methyl parathion remaining in treated samples of the commercial formulation of the insecticide were determined by high performance liquid chromatography (HPLC) using a Shimadzu (Kyoto, Japan) model 20A chromatographic system coupled to a model SPD-20A UV detector and fitted with a Varian (Agilent Technologies, Santa Clara, CA, USA) Pursuit 5 C_{18} reverse phase column (250 × 4.6 mm i.d.). The column temperature was held at 40 °C, the mobile phase comprised a 60:40 (v/v) mixture of water and acetonitrile (HPLC grade reagent; J.T Barker, Avantor Performance Materials, Center Valley, PA, USA), elution was isocratic at a flow rate of 0.8 mL min^{-1}, and UV detection was at 273 nm. The concentration of analyte was determined by reference to a calibration curve constructed using analytical standard grade methyl parathion. In order to identify possible intermediates formed during electrochemical degradation of the analytical standard, the HPLC system was coupled to a Shimadzu model SPD-M20A photodiode array detector (PAD) and operated under the chromatographic conditions outlined above.

The removal of organic material by electrochemical degradation of the commercial formulation of the insecticide was monitored using a Shimadzu model TOC-VCPN PC-controlled TOC analyzer.

2.5. Toxicity assays

Toxicity against the gram-negative marine bioluminescent bacterium *Vibrio fischeri* (GLX8400 lyo 5) of electrolyte containing the commercial formulation of methyl parathion was assessed before and after electrochemical degradation. Samples of electrolyte were treated with NaCl solution (20 g L^{-1}) and brought to a conductivity of 50 mS cm^{-1} prior to analysis. Starting from the concentration of the sample, eight consecutive dilutions (dilution factor 1:2) were prepared and the bioluminescence at 490 nm of the assay mixture containing the bacterium was determined after 5 and 15 min incubation at 15 °C using a LUMIStox 300 bench top luminometer (Dr. Lange, Düsseldorf, Germany). Half-maximal effective concentration (EC_{50}) values were calculated from the dose–response curves.

3. Results and discussion

3.1. Electrochemical characterization of methyl parathion

Chronoamperometric analysis of methyl parathion (analytical standard grade) in 0.1 M H_2SO_4 were conducted at different potentials within the region of stability of the electrolyte and of water decomposition. At potentials lower than that required for oxygen evolution (i.e. <1.5 V vs Ag/AgCl), the current did not increase in the presence of analyte (data not show), or of increased concentrations thereof, indicating that methyl parathion was not oxidized under such conditions. At an applied potential of 2.0 V vs Ag/AgCl, however, a rapid increase in current was observed (data not shown), while at 2.5 V vs Ag/AgCl, the current in the presence of analyte was considerably greater than that of the electrolyte alone and increased with increasing concentration of analyte (Fig. 1). The chronoamperogram also showed that the initial current decayed rapidly with time and maintained a steady state thereafter, a behavior that can be assigned to mass-transfer processes with continuous oxidation of analyte. It was concluded, therefore, that high values of current density would be required to oxidize methyl parathion.

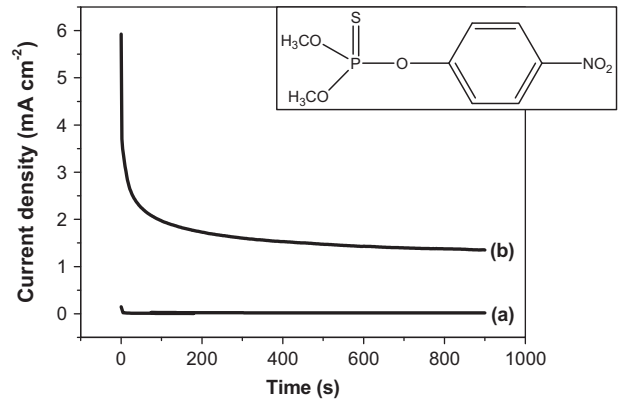

Fig. 1. Chronoamperograms obtained using a boron-doped diamond/Ti anode showing the supporting electrolyte (0.1 mol L^{-1} H_2SO_4) (a) and electrolyte containing analytical standard grade methyl parathion (insert) at a concentration of 100 mg L^{-1} (b). Experiments were conducted at 25 °C, the applied potential was 2.5 V vs Ag/AgCl (3 M) and solutions were stirred continuously.

3.2. Electrochemical degradation of methyl parathion

Current density is a fundamental parameter in electrochemical methods of treatment. Chronoamperometry revealed that values of current density >1.0 mA cm^{-2} would be required to oxidize methyl parathion. Thus, in order to investigate the effect of this parameter on the oxidation of the pesticide, current densities of 5, 10, 25, 50 and 100 mA cm^{-2} were applied and the efficiency of degradation determined under each of these conditions.

Fig. 2A–C depict the UV–VIS spectra of electrolyte solutions containing the commercial formulation of methyl parathion displayed as a function of time in electrolysis at applied current densities of, respectively, 5, 50 and 100 mA cm^{-2}. The bands at 277 nm are associated with $\pi \rightarrow \pi^*$ transitions in organic components with conjugated double bonds, and the intensities of absorption at this wavelength can be related to the concentrations of such constituents remaining in the electrolyte. At 277 nm, the spectral behavior was similar at all applied current densities, but the decay in absorbance was more pronounced as i_{appl} increased. In contrast, absorbance within the range 330–400 nm increased with time in electrolysis and applied current density, and such increase was particularly evident at 50 mA cm^{-2}. At 100 mA cm^{-2}, absorbance in the range 330–400 nm increased up to 90 min of electrolysis, following which the absorbance decreased. These findings indicate the formation of intermediates and/or byproducts, such as 4-nitrophenol, in the electrochemical degradation of methyl parathion.

Electrolysis at an applied current density of 5 mA cm^{-2} resulted in a decay in absorbance at 277 nm of 25.2% after 180 min of reaction. In contrast, a 73.4% decay in absorbance at this wavelength was achieved in the same reaction time when i_{appl} was100 mA cm^{-2}, indicating that mass transport affords better efficiency in the removal of methyl parathion.

Fig. 3A and B display HPLC-UV chromatograms of electrolytes containing the commercial insecticide recorded after 0, 60 and 180 min of electrolysis at applied current densities of, respectively, 50 and 100 mA cm^{-2}. The chromatographic profiles at the start of the experiment showed peaks associated with the electrolyte [retention time (R_t) = 3.40 min], with methyl parathion (R_t = 10.70 min), and with other components present in the commercial preparation (R_t = 3.59, 4.86 and 5.66 min). The intensity of the peak at 10.70 min diminished with respect to time of electrolysis at all values of i_{appl}, but at 5 mA cm^{-2} the decrease was 30.0% while at 100 mA cm^{-2} the reduction was 81.2%.

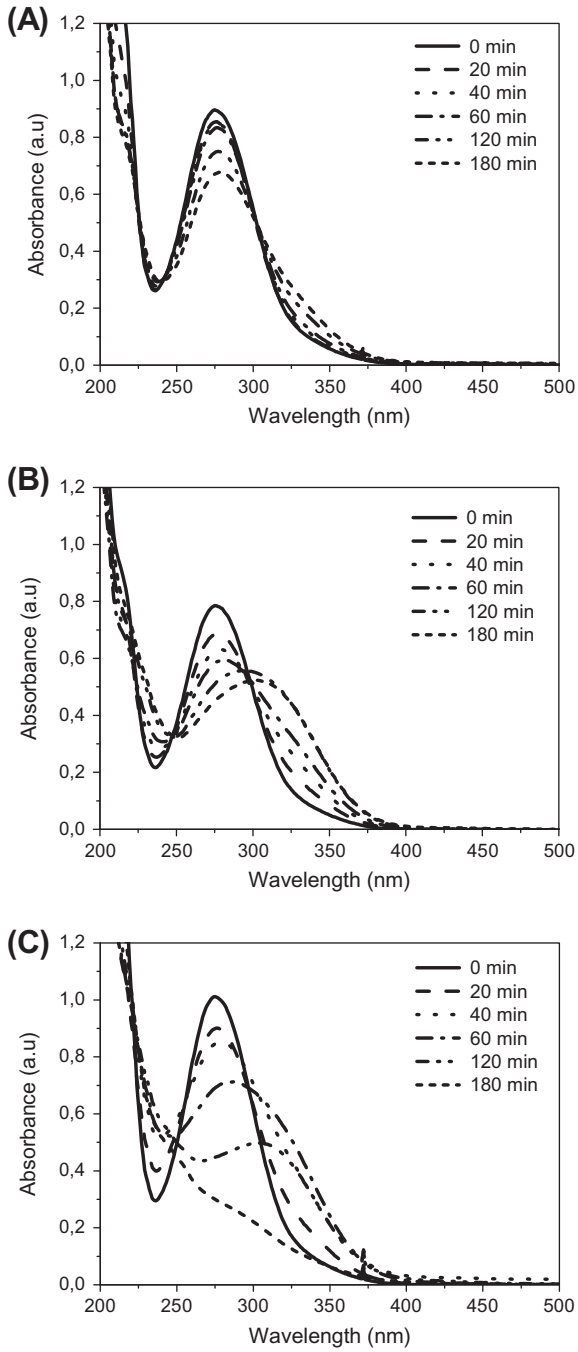

Fig. 2. UV–VIS spectra recorded during the electrochemical oxidation of a commercial formulation of methyl parathion using a boron-doped diamond/Ti anode with applied current densities of (A) 5 mA cm^{-2}, (B) 50 mA cm^{-2}, and (C) 100 mA cm^{-2}.

The orders of the reactions were determined from the equation:

$$\ln\frac{[MP]}{[MP]_0} = -k_{app}t \quad (1)$$

and the corresponding apparent rate constants (k_{app}) were obtained from the slopes of plots of relative concentration of methyl parathion ([MP]/[MP]$_0$) against time (Fig. 4). The reactions were considered pseudo-first order by virtue of the linearity of the plots (Table 1), and this kinetic behavior implies a constant formation of BDD (·OH) during the degradation process. Interestingly, the rate of electrochemical oxidation decreased as the applied current density was increased from 5 to 10 mA cm^{-2}, but the reaction rate showed incremental increases between applied current densities of 10 and 100 mA cm^{-2}.

The electrochemical degradation of analytical standard grade methyl parathion was monitored by HPLC-PAD in order to investigate the possible formation of intermediates and/or byproducts. The peak at 4.99 min that appeared in the chromatograms after 60 min of electrolysis at 50 mA cm^{-2} (Fig. 5A) was associated with a compound exhibiting an absorbance maximum at 314 nm (Fig. 5B). This peak was assigned to the degradation product, 4-nitrophenol, a compound that has been observed in various studies of the natural degradation of methyl parathion [23].

The degree of mineralization (i.e. conversion to CO_2) of methyl parathion achieved during the electrochemical degradation of the commercial insecticide was determined by TOC analysis (Fig. 6). Increased applied current density resulted in higher mineralization efficiency (ME; defined as the ratio of final to initial TOC values expressed as a percentage), which attained 67.6% at 100 mA cm^{-2}. The percentage of mineralization was lower than the percentage reduction in the concentration of methyl parathion, indicating that electrochemical degradation of the insecticide was accompanied by the formation of intermediates and/or byproducts.

The specific energy consumption (E_s) is a fundamental parameter in determining the efficiency of an electrochemical process. The value of E_s (kWh g^{-1}) relating to the electric power consumed per g of TOC removed may be calculated from:

$$E_s = \frac{E_{cel}\mathrm{it}}{1000\ \mathrm{m}} \quad (2)$$

where E_{cel} is the measured cell potential (V), I is the current applied (A), t is the time of electrolysis (h) and m is the amount of TOC removed (g) [13]. As shown in Fig. 6, values of E_s, as well as the amount of substrate converted to CO_2, increased with increased applied current density. It should be pointed out that the proposed treatment is promising because it does not require the presence of other oxidants (either added or produced electrochemically). Although anodic oxidation of organics in the presence of chlorinated species, such as NaCl or $NaClO_4$, may be associated with lower specific energy consumption, the likely generation of chlorinated intermediates or final products represents a significant limitation to the application of such methodology. Moreover, electrochemical processes carried out in the presence of chlorinated species can induce rapid breakdown of the diamond film.

At high current densities, the efficiency of the degradation process is reduced since various secondary anodic reactions may be favored, including the electrogeneration of H_2O_2 and O_3, and the formation of peroxodisulfate ($S_2O_8^{2-}$) from sulfate ions present in the supporting electrolyte. According to Michaud et al. [24], the formation of $S_2O_8^{2-}$ by anodic oxidation follows a mechanism whereby hydroxyl radicals, formed by water discharge at the anode:

$$H_2O \rightarrow {}^{\cdot}OH + H^+ + e^- \quad (3)$$

react with HSO_4^- from the supporting electrolyte:

$$2HSO_4^- + 2{}^{\cdot}OH \rightarrow S_2O_8^{2-} + 2H_2O \quad (4)$$

Peroxodisulfate ions can contribute to the oxidation of organic compounds, but the process is only efficient in the presence of high concentrations of H_2SO_4 and at high current densities.

Although electrochemical degradation would appear to represent an appropriate method for the removal of methyl parathion from contaminated waters, complete mineralization of the insecticide did not occur, and the formation of intermediates and/or byproducts was observed. Since such species may be toxic to a greater or lesser degree, toxicity bioassays of the treated electrolyte were performed in order to complete the evaluation

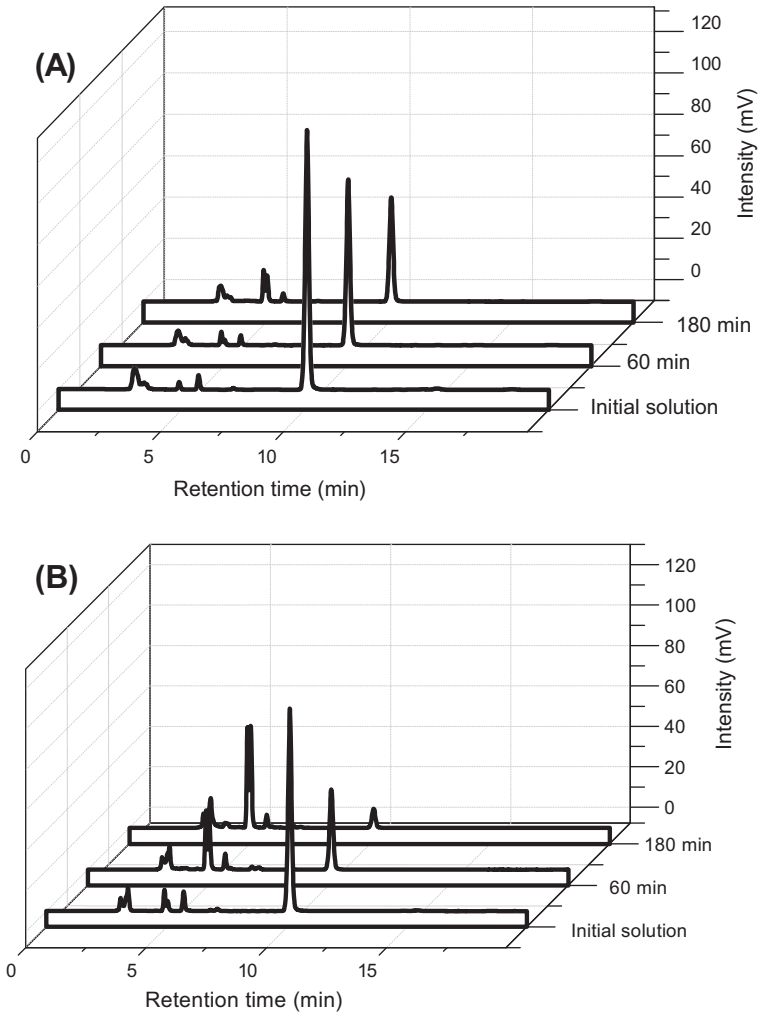

Fig. 3. HPLC/UV chromatograms recorded during the electrochemical oxidation of a commercial formulation of methyl parathion using a boron-doped diamond/Ti anode with applied current densities of (A) 50 mA cm^{-2}, and (B) 100 mA cm^{-2}.

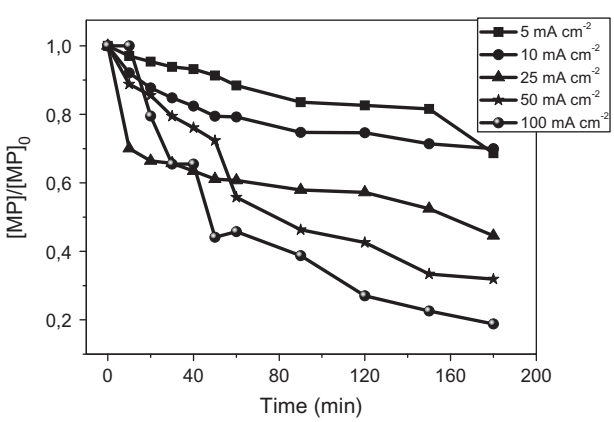

Fig. 4. Relative concentrations of methyl parathion vs time of electrolysis of a commercial formulation of methyl parathion using a boron-doped diamond/Ti anode with applied current densities of 5, 10, 25, 50 or 100 mA cm^{-2}.

Table 1
Apparent rate constants (k_{app}) for the electrochemical oxidation of methyl parathion using a boron-doped diamond/Ti anode at different applied current densities (i_{app}).

i_{app} (mA cm^{-2})	k_{app} [a] ($\times 10^{-3}$ min^{-1})	R [b]
5	1.40	0.98
10	1.16	0.98
25	1.70	0.99
50	2.38	0.97
100	7.30	0.97

[a] Determined from HPLC-UV analyses.
[b] Correlation coefficients.

of the proposed electrochemical treatment. As shown in Table 2, electrochemical degradation at an applied current density of 5 mA cm^{-2} increased the EC_{50} value of the original electrolyte towards the bioluminescent bacterium *V. fischeri*, although the effect was more pronounced at the higher current density where mineralization was greater.

It is important to note that the BDD film retained its original quality and crystalline appearance throughout all of the electrochemical experiments conducted in this study. The absence of delimitations or cracks in the diamond film demonstrates the high adherence of the film to the Ti substrate, a characteristic that is attributable to the optimization of the experimental parameters employed in the CVD method.

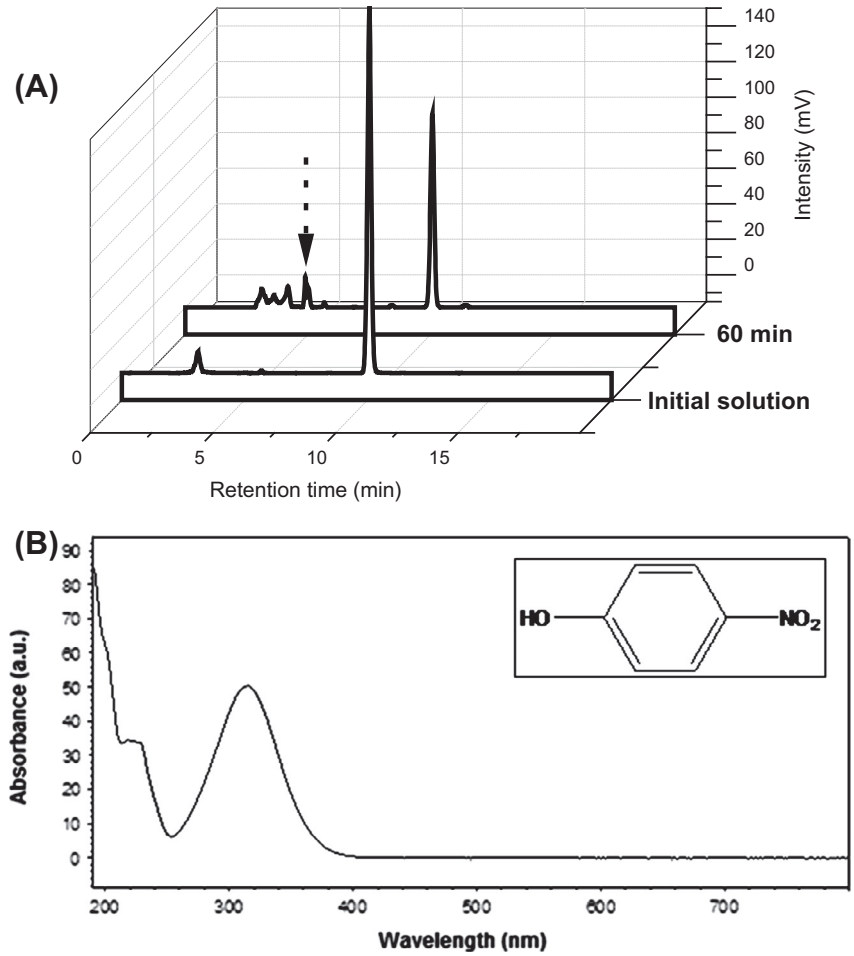

Fig. 5. (A) HPLC/PAD chromatograms recorded during the electrochemical oxidation of analytical standard grade methyl parathion (60 mg L^{-1}) using a boron-doped diamond/Ti anode with an applied current density of 50 mA cm^{-2}. (B) UV–VIS spectrum of a component of the treated electrolyte with retention time 4.99 min, subsequently identified as 4-nitrophenol (insert).

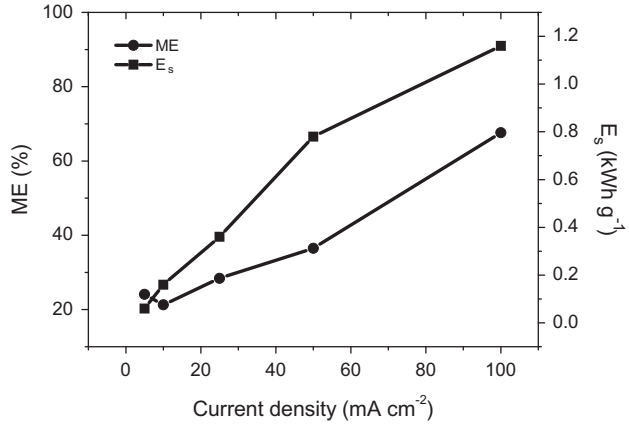

Fig. 6. Mineralization efficiency (ME) and specific energy consumption (E_s) plotted as functions of applied current density in the removal of methyl parathion by electrochemical degradation using a boron-doped diamond/Ti anode.

4. Conclusions

Electrochemical degradation using BBD/Ti electrodes represents an appropriate method for the removal of methyl parathion from contaminated waters. Chronoamperometry showed that significant oxidation of the insecticide commenced at 1.8 V vs Ag/AgCl.

Table 2
Toxicity against the gram-negative marine bioluminescent bacterium *Vibrio fischeri* of an electrolyte containing a commercial formulation of methyl parathion determined before and after electrochemical treatment at different applied current densities.

Sample	Relative toxicity (%)[a]
Original electrolyte	100
Electrolyte after treatment at 5 mA cm^{-2}	82.15
Electrolyte after treatment at 100 mA cm^{-2}	74.06

[a] Relative toxicity calculated as: [(initial EC_{50}/final EC_{50}) × 100].

Spectroscopic studies revealed that the intensity of absorbance at 277 nm decreased during the electrolysis of a commercial formulation of the methyl parathion at applied current densities between 5 mA cm^{-2} and 100 mA cm^{-2}. Chromatographic analysis demonstrated that 30.0% of the insecticide was removed after 180 min of electrolysis at a current density of 5 mA cm^{-2}, while 81.2% was degraded at 100 mA cm^{-2}. Mineralization efficiency increased with increased current density and attained a maximum value of 67.6% at 100 mA cm^{-2}. Specific energy consumption presented a similar behavior with a maximum value of 1.16 kWh g^{-1}. The EC_{50} value of the original solution of commercial insecticide against *V. fischeri* was increased after electrochemical treatment at an applied current density of 5 mA cm^{-2}, but the effect was more pronounced at 100 mA cm^{-2}.

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