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Original article

Electrochemical behavior and analytical detection of Imidacloprid insecticide on a BDD electrode using square-wave voltammetric method

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ABSTRACT

A sensitive square-wave voltammetric method for the determination of Imidacloprid (IMD) was developed using electrochemically pretreated boron-doped diamond (BDD) electrode. Aqueous solutions were prepared with Confidor 200 SL as the commercial formulation of IMD. Sodium sulfate (Na_2SO_4) was used as supporting electrolyte. The influence of operating parameters, such as the pH of the medium, frequency, pulse amplitude, scan increment and the concentration of IMD was investigated. An irreversible cathodic peak, corresponding to the reduction of IMD is observed at -1.21 V (*vs.* SCE) and the electrode reaction was controlled by adsorption. Under optimized conditions, the square-wave reduction peak current was linear over the concentration range of (30–200 μmol L^{-1}) with a detection and quantification limits of 8.60 μmol L^{-1} and 28.67 μmol L^{-1}, respectively. The results were compared with spectrophotometry and HPLC methods under some conditions and found to be in good agreement. To investigate applicability to real samples, the proposed method was applied to the determination of IMD in plum juice.

1. Introduction

Imidacloprid (*E*)-1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine (Fig. 1) is one of the most used neonicotinoid for the crop protection worldwide due to its low soil persistence and high insecticidal activity at a very low application rate [1]. It acts as antagonist by binding to postsynaptic nicotinic receptors in the insect's central nervous system resulting in the paralysis and death of insects [2]. IMD is the active substance of many commercial insecticides such as Confidor, Gaucho, Prestige, Admire, and Provado [3]. However, the intensive use of this insecticide in agriculture and the improper storage is a source of contamination of the environment. For these reasons, a range of methods have been utilized for the detection and quantification of IMD, such as high performance liquid chromatography [4–7], spectrophotometry [8], spectrofluorimetry [9,10], capillary electrophoresis [11], micellar electrokinetic chromatography [12] and enzyme-linked immunosorbent assay (ELISA) [13]. However, these methods suffer from some disadvantages such as high cost, long analysis time and requirement for sample pretreatment when some procedures as derivatization, extraction and purification are usually included.

Electroanalytical processes have been successfully applied for the determination of inorganic and organic compounds, including pesticides, in many environmental matrices, due to their good sensitivity, short time analysis, low-cost, and the possibility of sample analysis without extractions or pretreatments [14–16]. Several electrode materials such as glassy carbon [17], modified glassy carbon electrode [18,19], carbon paste [20], modified carbon paste electrode [21,22], carbon ceramic [23], bismuth modified electrode [24], modified silver electrode [25], and dropping mercury electrode [26,27], were used as cathodes for the detection and quantification of this insecticide.

Differential pulse polarography and square-wave adsorptive stripping voltammetry were used for the determination of IMD at hanging mercury drop electrode [26,27]. Two reduction peaks were observed in large pH ranges in both methods. The first peak corresponds to a four-electron transfer to give the hydroxylamine

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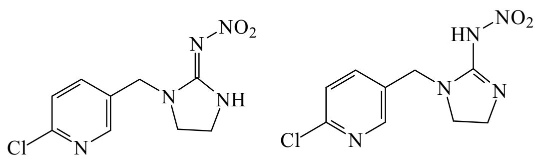
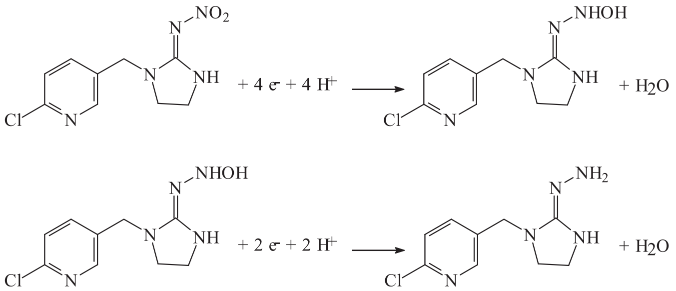


Fig. 1. Mesomeric form of imidacloprid.



Scheme 1. Proposed mechanism of IMD reduction at a mercury electrode [26,27].

derivative and the second correspond to a two electron-transfer to give the corresponding amine (Scheme 1). The limits of detection (LOD) were 0.01 μmol L^{-1} and 0.02 μmol L^{-1}, respectively.

Voltammetric determination of IMD at glassy carbon electrode has been reported [17]. The reduction peak is observed at high scan rate of 500 mV s^{-1}. The reported detection limit was 30.11 μmol L^{-1}, which is too high for carrying out trace analysis. Differential pulse voltammetry (DPV) determination of IMD at carbon paste electrode has been reported [20] with the LOD as 2.04 μmol L^{-1}. A copper(II) phthalocyanine modified carbon ceramic electrode fabricated by a sol–gel method [23], and a nano silver-Nafion/TiO_2-Nafion composite modified GCE [19], were used for the detection of IMD by DPV technique, with the LOD 0.28 μmol L^{-1} and 0.25 μmol L^{-1}, respectively for both electrodes. Recently, Lei *et al.* [18] describe a method for the determination of IMD on a GCE modified with poly(carbazole)/chemically reduced graphene oxide. This modified electrode was used as a sensing electrode for the detection of IMD. CV and DPV were used as sensing techniques. The LOD and LOQ values of CV are 0.22 μmol L^{-1} and 0.74 μmol L^{-1}, respectively, while those values of DPV are 0.44 μmol L^{-1} and 1.52 μmol L^{-1}, respectively. The LOD and LOQ for the reduction of IMD on various electrodes are presented in Table 1.

None of the previously conducted research works reports the electrochemical determination of the IMD on boron-doped diamond (BDD) electrode. The development of a novel electrochemical technique using BDD electrode can furnish the priceless services in the monitoring of the compounds that are important in terms of human health defense, environment and food chemistry. BDD electrodes have been excellently used as an alternative to other conventional electrodes (*e.g.*, glassy-carbon or platinum electrodes) and are particularly attractive in electroanalytical applications for pesticides [28–35]. It has several important characteristics such as an inert surface with low adsorption proprieties, remarkable corrosion stability, even in strong acidic media, an extremely wide potential window in aqueous solutions (up to 3.5 V) and high reproducibility of electrochemical responses [36–39].

The aim of this work is to develop a simple, fast and sufficiently sensitive electroanalytical methodology for the detection and quantification of IMD in the commercial formulation (Confidor 200 SL) using square-wave voltammetry at a BDD electrode. The results of the developed electroanalytical method were compared with the UV spectrophotometric and HPLC methods.

2. Experimental

Reagents: All solutions containing different amounts of IMD taken from an emulsifiable concentrate (Confidor 200 SL Bayer Crop Science) containing 200 g L^{-1} IMD were prepared with ultrapure water. These solutions were kept in the dark at 4 °C. The supporting electrolyte was sodium sulfate (Na_2SO_4) 0.05 mol L^{-1} provided by Biochem. Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were supplied by Merck and added to the required pH values covering the pH range of 3.0–11.0. Before each experiment, the solution was purged with nitrogen for 5 min to remove oxygen and kept away from any agitation to achieve a balance between the electrodes and the solution.

Apparatus: Square-wave voltammetry measurements were performed using a potentiostat–galvanostat (VoltaLab PST050), and a conventional three-electrode cell at 25 °C. BDD was used as working electrode for voltammetric experiments. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The BDD electrode (0.07 cm^2) was provided by the Swiss Center for Electronics and Microtechnology (CSEM). It was synthesized by the hot filament chemical vapor deposition technique (HF-CVD) on single-crystal *p*-type Si ⟨1 0 0⟩ wafers (1–3 mΩ cm, Siltronix) [40]. The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm. In order to obtain an active surface and reproducible electrochemical response, the BDD electrode was subjected to potential cycling conditions in 0.05 mol L^{-1} sodium sulfate between −3.0 V and +3.0 V at a high scan rate of 5.0 V s^{-1} for

Table 1
Comparison of analytical parameters for the determination of IMD on various electrodes.

Method	Electrode	Linear range (μmol L^{-1})	LOD (μmol L^{-1})	LOQ (μmol L^{-1})	References
DPP	HMDE	0.039–0.782	0.01	–	[27]
SWASV		0.02–0.50	0.02	–	[26]
CV	GCE	10.9–1956	30.1	101.6	[17]
DPV	CPE	6.7–117.4	2.04	6.8	[20]
CV		1–7	0.63	2.1	
DPV	$n\mathrm{Ag}n_f/n\mathrm{TiO}_2n_f$/GCE	0.5–3.5	0.25	0.83	[19]
Amperometry		1–5	0.93	3.1	
SWV	Hg(Ag) FE	3.55–185.6	1.05	3.55	[25]
CV	PCz/CRGO/GCE	3–10	0.22	0.74	[18]
DPV		3–10	0.44	1.52	
DPV	BiFE	9.5–200	2.9	–	[24]
SWV	BDD	30–200	8.6	28.6	This work

HMDE, hanging mercury drop electrode; GCE, glassy carbon electrode; CPE, carbon-paste electrode; $n\mathrm{Ag}n_f/n\mathrm{TiO}_2n_f$/GCE, nanosilver Nafion®/nanoTiO_2 Nafion® modified glassy carbon electrode; Hg(Ag) FE, Silver-amalgam film electrode; PCz/CRGO/GCE, poly(carbazole)/chemically reduced graphene oxide modified glassy carbon electrode; BiFE, Bismuth-film electrode; BDD, Boron-Doped Diamond.