

ELECTROCHEMICAL DETECTION OF PARAQUAT FROM WATER USING PLATINUM MODIFIED BDD ELECTRODE

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Abstract

Voltammetric and amperometric detection of paraquat (PQ) herbicide from aqueous solutions has been successfully achieved using a boron-doped diamond (BDD) electrode modified with platinum particles. Electrochemical deposition of platinum was performed by chronoamperometry technique operated at two potential levels, *i.e.*, -0.15 V for 1 s and 0.1 V for 6s. Operational parameters of electrochemical techniques tested in detection application were determined in order to achieve superior electroanalytical performances for quantitative assessment of paraquat concentration at trace level. Both cyclic voltammetry and multiple-pulsed amperometry exhibited best electroanalytical performances in terms of sensitivity and lowest detection limit, in comparison with the other applied voltammetric pulsed techniques.

Introduction

Paraquat (PQ) is a very toxic biquaternary ammonium compound usually synthesized as dichloride salt (Fig. 1). PQ is used as a quick-acting herbicide that destroy non-selectively the green plants by direct contact or by translocation within the plant [1]. PQ is adsorbed rapidly into soil, especially in the clay mineral lattice sheet, and then, it arrives into groundwater easily by leaching due to its high solubility of 620 g/L at 25 °C [1]. This compound have a long persistence into environment due to its non-biodegradability. Its toxicity affect all living organisms, and the accidental or deliberate ingestion could be lethal or cause acute poisoning [2].

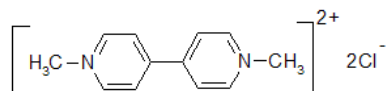


Figure 1. Structural formula of Paraquat

In European Union (EU) this pesticide was banned since 2007, but it is still used in nearly 90 countries all over the world in tobacco, apples, citric fruits, and other around 100 crops [3]. Several publications have been focused on the quantification of the organochlorine residue presence, including paraquat, in surface waters, sediments, biota and vegetation [4,5].

Electrochemical techniques could represent a simple, fast and sensitive alternative for the quantitative assessment of paraquat from water.

The aim of this paper is to modify a BDD electrode with platinum particles in order to obtain a sensitive sensor able to detect paraquat at very low concentration, up to 10⁻⁹ M. Cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), square-wave voltammetry (SWV) and multiple pulse amperometry (MPA) were assessed in order to find the best operational condition for paraquat detection from water.

Experimental

A commercial BDD electrode, provided by Windsor Scientific has been modified with platinum particles by electrochemical deposition. Platinum electrodeposition was performed in galvanostatic regime, through chronoamperometry technique operated at two potential levels, the first of -0.15 V for 1 s and the second of 0.1 V for 6s and Pt-modified electrode was obtained, named BDD-Pt. All the electrochemical experiments were performed using an Autolab potentiostat/galvanostat PGSTAT 302 (EcoChemie, The Netherlands), with a standard three electrode cell with the BDD-Pt as working electrode, platinum sheet as counter electrode and saturated calomel electrode as reference electrode. Solution of 0.1 M sodium sulfate (Merck) and 1 mM PQ (Pestanal, Sigma-Aldrich) were freshly prepared with distilled water.

Results and discussion

Cyclic voltammetry

The first electrochemical technique used in order to characterize the behavior of BDD-Pt electrode in the presence of PQ and also, as electrochemical detection method was cycling voltammetry. The tests were performed in 0.1 M Na₂SO₄ supporting electrolyte, in the potential range between -1.25 V/SCE and 0 V/SCE. The reduction process of PQ occurred at the potential value of -0.72 V/SCE, and the useful cathodic signal increased with the PQ concentration from 0.2 μM to 1.2 μM. At higher concentration, a fouling of the electrode surface was noticed, probably due to the formation of an insulating layer on the electrode active surface.

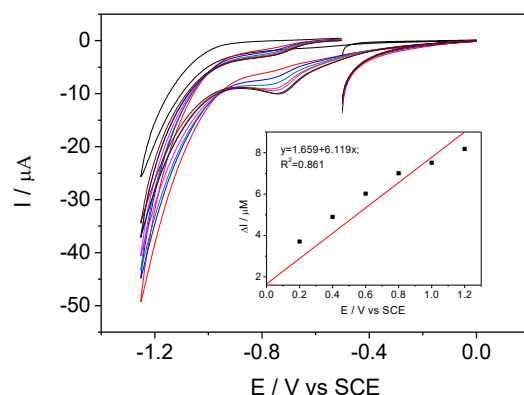


Figure 1. Cyclic voltammograms (CVs) recorded on BDD-Pt electrode in 0.1 M Na₂SO₄ supporting electrolyte (1) and in the presence of different PQ concentrations: 1-0 mM; 2-0.2 μM; 3-0.4 μM; 4-0.6 μM; 5-0.8 μM; 6-1.0 μM; 7-1.2 μM; 8-1.4 μM, scan rate: 50 mV·s⁻¹. Inset: Calibration plot of dependence between cathodic peak current recorded at potential of -0.73 V vs SCE on BDD-Pt electrode and PQ concentration.

Pulsed Voltammetric Techniques

Taking into account the advantages of pulsed-voltammetric techniques, *e.g.*, rapid analyses time, increased useful signal minimized effect of the background noise and good reproducibility, differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) were tested at different operational parameters in order to select the optimum conditions. The chosen operation parameters for DPV were: scan rate (*v*) of 50 mV·s⁻¹, step potential (SP) of 10 mV, modulation time (Mt) of 0.1 s and modulation amplitude (MA) of 25 mV. Despite of the lower sensitivity value recorded by DPV on BDD-Pt electrode in comparison with the other tested techniques for PQ electrochemical quantification, no electrode fouling occurred in the concentration range of

0.2 μM - 5.0 μM , and a well-defined PQ reduction peak can be observed at the potential of -0.69 V/SCE (Fig. 2).

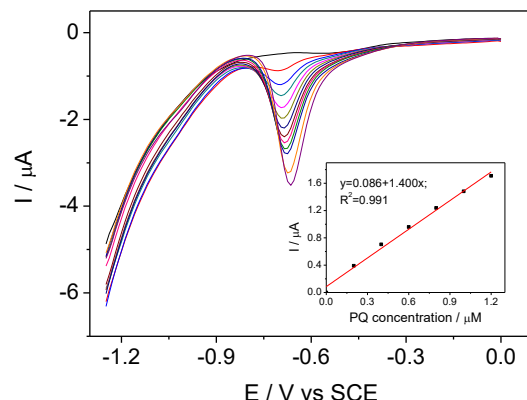


Figure 2. Differential-pulsed voltammograms recorded on BDD-Pt electrode in Na_2SO_4 0.1 M supporting electrolyte (1) and in the presence of different PQ concentrations: 2-0.2 μM ; 3-0.4 μM ; 4-0.6 μM ; 5-0.8 μM ; 6-1.0 μM ; 7-1.2 μM ; 8-1.4 μM ; 9-1.8 μM ; 10-2.0 μM ; 11-3.0 μM ; 12-4.0 μM ; 13-5.0 μM . Inset: calibration plot of cathodic peak current vs PQ concentration.

SWV was performed in three different operational parameter conditions, and better electroanalytical performances for this technique were recorded at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$, a frequency of 25Hz, a step potential of 4mV and an amplitude of $A=50\text{mV}$ (Table 1).

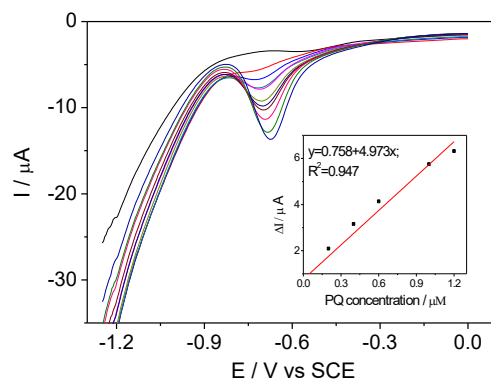


Figure 3. Square-wave voltammograms recorded on BDD-Pt electrode in 0.1 M Na_2SO_4 supporting electrolyte (1) and in the presence of different PQ concentrations: 2-0.2 μM ; 3-0.4 μM ; 4-0.6 μM ; 5-0.8 μM ; 6-1.0 μM ; 7-1.2 μM ; 8-1.4 μM ; 9-1.8 μM ; 10-2.0 μM ; 11-3.0 μM ; 12-4.0 μM . Inset: calibration plot of cathodic peak current vs PQ concentration.

Among amperometric techniques, multiple-pulsed amperometry (MPA) was tested in this paper in order to achieve better electroanalytical performances for PQ detection. The lowest detection limit of 3.9 nM was achieved by this technique at an applied potential of -0.72 V/SCE. The electrode sensitivity was superior to the pulsed-voltametric techniques, but equal to the one recorded by cyclic voltammetry (Table 1). The role of *in-situ* cleaning step is envisaged by the recorded enhanced useful signal during continuous amperometric detection of PQ by MPA.

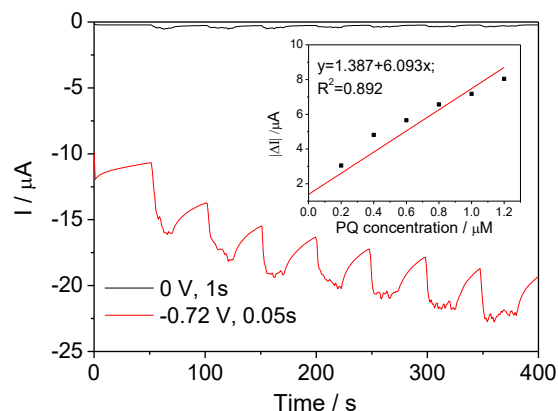


Figure 4. Multiple-pulse amperogram recorded on BDD-Pt electrode in 0.1 M Na₂SO₄ supporting electrolyte (1) and in the presence of different PQ concentrations: 2-0.2 μM; 3-0.4 μM; 4-0.6 μM; 5-0.8 μM; 6-1.0 μM; 7-1.2 μM; 8-1.4 μM. Inset: calibration plot of anodic peak current recorded at potential of -0.72 V/SCE vs PQ concentration.

Table 1. Electroanalytical performances recorded for PQ detection

Technique	Conc. range (μM)	Parameters	E / V	Sensitivity m (μA/μM)	LOD (μM)	LOQ (μM)	R ²
CV	0.2-1.2	0.05 V/s	-0.73	6.119	0.0041	0.0137	0.861
DPV	0.2-1.2	Mt=0.05s; It=0.1s; MA=25 mV; sp=10 mV	-0.69	1.400	0.0157	0.0523	0.991
SWV	0.02-1.22	F=50Hz, SP=4mV; A=85mV	-0.69	4.086	0.0144	0.0480	0.995
SWV	0.2-1.2	F=25Hz; SP=4mV; A=50mV	-0.71	4.973	0.0073	0.0244	0.947
MPA	0.2-1.2	0V, 1s; -0.72V, 0.05s	-0.72	6.093	0.0039	0.0128	0.892

Conclusion

BDD-Pt modified electrode was successfully applied for detection of trace amount of PQ in aqueous solution. All voltammetric and amperometric techniques exhibited useful features for PQ detection from water, with very high sensitivity and low limits of detection (LOD) and quantification (LOQ) in the optimal determined conditions of CV and MPA technique.

Acknowledgements

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