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Square wave voltammetric determination of diquat using natural phosphate modified platinum electrode

H. El Harmoudi ^{a,b}, M. Achak ^{a,b}, S. Lahrich ^a, A. Farahi ^{a,b}, L. El Gaini ^b,
M. Bakasse ^b, M.A. El Mhammedi ^{a,*}

^a *Equipe d'Analyse des Micropolluants Organiques, Faculté de Sciences, Université Chouaib Doukkali, Morocco*

^b *Equipe de Chimie Analytique et Modélisation Statistique, Université Hassan 1^{er}, Faculté Polydisciplinaire, BP: 145, Khouribga, Morocco*

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Abstract A platinum electrode modified with natural phosphate (NP) was evaluated as an electrochemical sensor for diquat (DQ) in aqueous medium. The electrode was prepared by the deposition of natural phosphate on the platinum surface. Diquat was preconcentrated on the surface of the modified electrode by adsorbing with natural phosphate and reduced at a negative potential in 0.1 M K₂SO₄ solution. The influence of accumulation time and pH of the electrolytic solution were investigated. The calibration graph obtained under the optimized conditions was linear with a correlation coefficient of 0.9813 at levels near the detection limits up to at least 5.32×10^{-9} mol L⁻¹ with the relative standard deviation (RSD) lower than 3.37%. Interferences by some metals were investigated. Fe, Zn, Cu, MnO₄ and Hg apparently affected the peak currents *P*₁ and *P*₂ of diquat. The natural phosphate modified platinum electrode was applied to the determination of diquat in natural water samples. The results indicate that this electrode is sensitive and effective for the determination of diquat.

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1. Introduction

Diquat is still largely used for preharvest desiccation and weed control of various crops, and as really interesting materials for investigating novel chemically-modified electrochemical systems, owing to their reversible and electrocatalytic behavior

(Murray, 1984; Bird and Kuhn, 1981). The incidence of diquat poisoning, often through suicidal intent rather than accidental ingestion, is still a major problem in many countries. Because of its acute toxicity to mammals and humans (Vale et al., 1987), the quantitative analysis of these compounds, and especially residue analysis, are of prime interest.

Several methods based on different analytical techniques have been reported for the determination of diquat; i.e. Liquid chromatography–electrospray ionization mass spectrometry (MRM) (Aramendía et al., 2006), Solid-phase extraction (SPE) (Grey et al., 2002), Fluorescence and Raman spectroscopy (Carrillo-Carrión et al., 2011), High performance liquid chromatography (HPLC) (Chiaki Fuke et al., 2002; Zougagh et al., 2008), Capillary electrophoresis (CE) (Núñez et al.,

* Corresponding author. Tel.: +212 68858296; fax: +212 23485201.

E-mail address: elmhammedi@yahoo.fr (M.A. El Mhammedi).

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2001) and kinetic-spectrophotometric method (Díaz et al., 2002). Most of these methods are unsuitable for on-site screening, however, because of their size, cost, and the time required to perform the analysis. There is, therefore, an urgent need for a simple, relatively cheap, sensitive, and reliable method for on-site measurement of toxic compounds in many areas of application, for example biomedical, natural and industrial samples. Therefore a fast and accurate analytical method for the estimation of diquat exposure has been necessary.

In the last years, the use of an electrode modified chemically by different types of organic and inorganic compounds has been one of the most promising areas of analytical sciences (Chen et al., 2006; Yeh and Wang, 2006; Kotkar and Srivastava, 2006). The greatest interest in the use of a chemically modified electrode is due to its capacity to act as a redox mediator, increasing the charge transfer between the electrode and the redox species, thus promoting an improvement in the analytical sensitivity (Leznoff and Lever, 1989).

More specifically, the electrochemical detection of diquat has been performed on different electrode surfaces, including solid electrodes (El Mhammedi et al., 2008, 2009), dental amalgam electrode (DAE) (Melo et al., 2009) and mercury electrode (Walcarius and Lamberts, 1996). This electroanalytical technique is thus less sensitive to the effects of matrix interferences, a property which characterizes its success in electroanalysis (Melo et al., 2009; Kalcher et al., 2009).

This paper describes a square wave voltammetric (SWV) procedure for the determination of traces of diquat by using a natural phosphate film coated platinum electrode (NP-Pt). The interference of some common heavy metal ions, such as Fe, Zn, Cu and Hg was investigated. The performance of analytical method and the NP-Pt/DQ interaction was investigated using cyclic voltammetry, square wave voltammetry and electrochemical impedance spectroscopy. Some experimental conditions were optimized and a voltammetric method for the determination of diquat in natural water was proposed and the result was satisfactory.

2. Experimental

2.1. Reagent

Diquat, potassium sulfate, and nitric acid were of analytical grade and from Aldrich. Standard metal solutions of mercury, zinc, iron and copper nitrates were purchased from Fisher Scientific. A natural phosphate (NP) used in this work was obtained in the Khouribga region (Morocco) (El Mhammedi et al., 2007). Stock solutions of diquat were prepared by dissolving diquat in deionized water (DW). All preparations and dilution of solutions were made with deionized water.

Provisions were made for oxygen removal by bubbling the solution with azotes gas for about 5 min then the solution was blanketed with azotes gas while the experiment was in progress. For reproducible results, a fresh solution was made for each experiment.

2.2. Instrumental

Electrochemical measurements were performed using a voltmeter potentiostat (model PGSTAT 402, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose

electrochemical systems data processing software (votalab master 4 software) connected to a Pentium IV computer run under windows 98 and a conventional three electrode cell. All voltages were reported with respect to Ag/AgCl (3 M KCl) reference electrode, Platinum was used as the auxiliary electrode and NP-Pt as a working electrode.

The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values. The coated specimen was examined using a scanning electron microscope (SEM, Jeol JSM-5500).

2.3. Electrode preparation

Prior to all measurements, the platinum plate, with a dimension of $0.5 \times 0.5 \text{ cm}^2$, was polished with a different emery paper up to 1200 grade, washed thoroughly with bidistilled water degreased and dried with acetone. The natural phosphate was treated by techniques involving attrition, sifting, calcinations (900°C), washing, and recalcination. Glycidoxypolytrimethoxysilane, and aminopropyltrimethoxysilane were mixed and diluted by water containing glycerol and ethanol to make a sol-gel paste to bind natural phosphate particles. A special NP-paste suspension was prepared by mixing the fine NP powder with the paste solution with a solid/liquid ratio of 2.0. The paste was spread on the platinum electrode for electrochemical studies. Deposits were heated at 25°C for 24 h.

2.4. Procedure

Under ambient conditions the platinum electrode modified with natural phosphate was immersed in a cell containing a standard solution of diquat and 20 mL of supporting electrolyte ($0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$). Meanwhile the solution was stirred by a 1.2 cm magnetic stirrer bar (rotating about 600 rpm) at open circuit to get the chemical deposition. Cyclic voltammetry was used to evaluate the electrochemical properties of the electrodes. To monitor the uptake and release of the analyte from the electrodes, square wave voltammetry was employed because of its better detection limit. The square wave voltammetry was recorded in the range from -0.3 V to -1.3 V , for which the scan rate is 1 mV s^{-1} , step potential 25 mV; amplitude 5 mV and duration 5 s. Optimum conditions were established by measuring the peak currents in dependence on all parameters. Electrochemical impedance spectroscopy (EIS) was carried out by the same three electrode-cell setup described above before and after the accumulation step. Impedance spectra were obtained in the frequency range between 100 kHz and 10 mHz with 10 points per decade at the potential of 0 V after 30 min of immersion in non-de-aerated solutions.

3. Results

3.1. Voltammetric and adsorptive characteristics of the diquat modifier complex

Scanning electron microscopy (SEM) was used to study the surface of a typical modified electrode. The result is shown in Fig. 1. Natural phosphate particle sizes can be seen to be between $\sim 1 \mu\text{m}$ and $\sim 20 \mu\text{m}$. This film was not disintegrated or detached from the surface when immersed in the electrolytic solution. The porosity of coating, especially the porosity

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