Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.jfda-online.com

Original Article

Electrochemical determination of paraquat in citric fruit based on electrodeposition of silver particles onto carbon paste electrode

Abdelfettah Farahi [a,b], *Mounia Achak* [c], *Laila El Gaini* [b], *Moulay Abderrahim El Mhammedi* [a,*], *Mina Bakasse* [b]

[a] *Laboratoire de Chimie et Modélisation Mathématique, Universite Hassan 1, 25 000 Khouribga, Morocco*

[b] *Laboratoire de Chimie Organique Biorganique et Environnement, Faculté de Sciences, Universite Chouaib Doukkali, El Jadida, Morocco*

[c] *Ecole Nationale des Sciences Appliquées, Laboratoire des Sciences de l'Ingénieur Pour l'Energie, Universite Chouaib Doukkali, El Jadida, Morocco*

ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form
2 March 2015
Accepted 31 March 2015
Available online 19 May 2015

Keywords:
citric fruit cultures
electrodeposition
paraquat
silver

ABSTRACT

Carbon paste electrodes (CPEs) modified with silver particles present an interesting tool in the determination of paraquat (PQ) using square wave voltammetry. Metallic silver particle deposits have been obtained via electrochemical deposition in acidic media using cyclic voltammetry. Scanning electron microscopy and X-ray diffraction measurements show that the silver particles are deposited onto carbon surfaces in aggregate form. The response of PQ with modified electrode (Ag-CPE) related to Ag/CP loading, preconcentration time, and measuring solution pH was investigated. The result shows that the increase in the two cathodic peak currents (Peak 1 and Peak 2), under optimized conditions, was linear with the increase in PQ concentration in the range 1.0×10^{-7} mol/L to 1.0×10^{-3} mol/L. The detection limit and quantification limit were 2.01×10^{-8} mol/L and 6.073×10^{-8} mol/L, respectively for Peak 1. The precision expressed as relative standard deviation for the concentration level 1.0×10^{-5} mol/L ($n = 8$) was found to be 1.45%. The methodology was satisfactorily applied for the determination of PQ in citric fruit cultures.

1. Introduction

Paraquat (1-1dimethyl-4-4-bipiridyl) is a biquaternary ammonium compound that is normally synthesized as the dichloride salt. It was introduced in the 1960s, and today it is used in > 100 countries in plantations of tobacco, apples, and other crops [1]. Paraquat (PQ) is very toxic to all living organisms, and many cases of acute poisoning and death have been reported over the past decade. Numerous studies suggest a

---

* *Corresponding author*. Laboratoire de Chimie et Modélisation Mathématique, Universite Hassan 1, Hay Ezzaitouna, BP 145, 25 000 Khouribga, Morocco.

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

http://dx.doi.org/10.1016/j.jfda.2015.03.003

link between exposure to PQ and an increased risk for developing Parkinson's disease (PD) [2]. This herbicide is structurally similar to MPP+ (1-methyl-4-phenylpyridinium), the active metabolite of MPTP (1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine), which is known to produce parkinsonian symptoms in drug users [3] and PD pathologies in animals [4]. In addition, a recent epidemiologic study shows the possible correlation between exposure to PQ and PD development in humans [5].

The main suggested potential mechanism for PQ toxicity is the production of superoxide radicals from the metabolism of PQ by microsomal enzyme systems, and by inducing mitochondrial toxicity [6]. Since July 2007, the use of this pesticide in the European Union (EU) has been banned; however, this does not preclude farmers outside the EU from continuing to use PQ and export their products to the EU. Therefore, PQ is included in the EU database between the compounds that should be monitored in food samples, and maximum residue limits have been established for different commodities [7]. Thus, for the case of citric fruit cultures, the maximum residue limit is 20 μg/kg [8]. The detection of PQ and herbicide residues in food samples is hampered owing to their particular physicochemical features and because this process requires the application of specific extraction and analytical procedures. The latter can be limited by interferences from food caused by a species with a similar structure (diquat), even at concentrations of the same order as PQ [9]. Currently, there is an urgent and specific increasing requirement for a more accurate and reliable detection method to cope with the more subtle adulterations in food. Several voltammetric methods have been developed to study the electrochemical behavior of PQ using dental amalgam and mercury [10], bismuth film [11], gold electrode [12,13], pyrolitic graphite [13], chemically modified carbon paste electrode (CPE) [14], and modified film electrodes [15–18]. The use of voltammetric methods has a considerable drawback that is related to the adsorption process of the analyte and/or the resulting products of the electrochemical reactions on the electrode surface. Indeed, low analytical sensitivities and reproducibility of the electroanalytical response were also observed [19,20]. The substantial versatility of carbon electrodes resides in their wide range of possible modifications. In fact, the electrode composition can be modified via the addition of different substances, such as metals, polymers, and enzymes [21–24]. The design of new nanoscale materials has acquired ever-greater importance in recent years owing to their various applications. Among these materials, metallic particles are of great interest because of their numerous properties [25,26]. Numerous methods describing the synthesis of metallic silver particles in solution as well as by deposition on solid surfaces have been presented. These include chemical synthesis by means of reduction with different reagents [27], UV light or electron beam irradiation [28], and electrochemical methods [29–32]. The latter provides an easy and rapid alternative for the preparation of metallic particle electrodes.

Recently, in our laboratory silver was used as a modifier of carbon paste, and we characterized these modified electrodes as sensing probes of PQ [33]. The used electrode was prepared by solid reaction between silver nitrates and carbon powder. However, the obtained silver was found to be supported heterogeneously as agglomerates onto the carbon paste. In this work, in order to overcome this problem, modified electrodes have been employed using the electrochemical deposition of silver from electrolytic solution. This methodology has been successfully applied to determine PQ in food samples, without any prepurification or preparation step of the sample. The modified electrode is compared with other related reports in the literature and is also independently tested with high-performance liquid chromatography (HPLC) toward the sensing of PQ in citric fruit cultures where good agreement is found.

2. Methods

2.1. *Reagents*

All chemicals used were of analytical grade or of the highest purity available. Sodium sulfate, sodium hydroxide, silver nitrate, acetic acid, and chloridric acid were obtained from Merck (Darmstadt, Germany), Fluka (St. Gallen, Switzerland), and Riedel de Haen (Seelze, Germany) Chemical Companies and were used as received. PQ ions (Sigma Aldrich, St. Louis, MO, USA) were dissolved in 0.1 mol/L Na_2SO_4 to prepare stock solutions of 1.0×10^{-3} mol/L. The working standard solutions were prepared by successive dilution of the stock solutions by sodium sulfate. Carbon paste was supplied from Carbone Lorraine (Lorraine, France; ref 9900). All other reagents used were of analytical grade. Distilled water was used throughout the preparation of the solutions.

2.2. *Instruments*

Cyclic and square wave voltammetry (SWV) were carried out with a voltalab potentiostat (model PGZ 100; Radiometer Analytical Inc., Hegnau, Switzerland) driven by the general-purpose electrochemical systems data processing software (voltalabmaster 4 software). The electrochemical cell was configured to work with three electrodes, using silver-modified carbon paste as the working platinum plate for counter and a system Ag/AgCl (3.00 mol/L) as reference electrodes. The pH meter (Radiometer, SENSION; PH3, Leganés, Spain) was used for adjusting pH values. X-ray diffraction studies of prepared powder Ag/CP were carried out using a diffractometer (XRD: Cu Ka radiation, XPERT-PRO). CuKα radiation ($\lambda = 1.5406$ nm) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 10° and 80° with a step size of 0.02° 2θ per second. Scanning electron microscopy (SEM) measurements were performed on an FEI Nova SEM (Philips) instrument with an AMETEK energy dispersive X-ray system (Nova 200) operated at an accelerating voltage of 30 kV. Imaging of solids deposited on the 3-mm GC electrodes was performed with the aid of a custom-built electrode holder. Prior to SEM imaging, samples were thoroughly rinsed with acetone and Milli-Q water and dried under a flow of nitrogen.

2.3. *Procedure*

We describe an easy procedure to obtain silver particle-modified CPE. The method is based on the electrochemical deposition of silver on CPE surface from Britton–Robinson