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Interaction study of paraquat and silver electrode using electrochemical impedance spectroscopy: Application in milk and tomato samples

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ABSTRACT

This paper reports on the use of electrochemical impedance spectroscopy (EIS) for analytical determination of paraquat herbicide at a silver electrode. The electrochemical technique was applied to aqueous solution, at pH 7.0, containing different concentrations of paraquat. The impedance measurements were carried out in the frequency range from 100 mHz to 100 KHz at a potential of 0.0 mV versus Ag/AgCl. The Nyquist plots were modeled with a Randle equivalent circuit, by identifying the charge transfer resistance as the relevant concentration dependent parameter. The silver surface adsorbs paraquat and the transfer process is controlled by diffusion. The response of the working electrode was attributed to the electron-exchange mechanism at the electrode–contact interface and the ion exchange at the electrode–solution interface. The proposed methodology offers good repeatability (RSD = 1.03%) with ($n = 8$) and impedimetric response to paraquat in the range from 1.0×10^{-14} to 8.0×10^{-4} mol L^{-1}. The detection limit (DL, 3σ) and quantification limit (QL, 10σ) were 7.37×10^{-16} mol L^{-1} and 24.59×10^{-16} mol L^{-1} respectively. The method was satisfactorily applied to determine paraquat in milk and tomato samples.

1. Introduction

Paraquat (PQ(II)) is a foliage contact herbicide with desiccant and defoliant action, used in the control of a variety of plants. The extensive use of PQ(II) produces major environmental problems since it is a highly toxic pollutant and causes death after large oral doses (>40 mg kg^{-1}) by producing multiorgan failure (Chen, Zhang, Sorani, & Giacomini, 2007). The toxicity of PQ(II) is essentially related to its quick reduction and subsequent reoxidation to produce reactive oxygen and nitrogen species (Dinis-Oliveira et al., 2006). PQ(II) is very toxic to all living organisms, and many cases of acute poisoning and death have been reported over the past decade. The main suggested potential mechanism for PQ(II) toxicity is the production of superoxide radicals from the metabolism of the PQ(II) by microsomal enzyme systems, and by inducing mitochondrial toxicity (Mohammadi-Bardboria & Ghazi-Khansarib, 2008). Moreover, the generation of reactive oxygen species (ROS) appears to play a critical role in pulmonary injury induced by pneumotoxic substances such as PQ (II). It is suggested that induced pulmonary injury involves the generation of PQ(II) cation radicals from redox cycling, resulting in the oxidation of nicotinamide adenine dinucleotide phosphate-oxidase (NADPH), to nicotinamide adénine dinucléotide phosphate (NADP+) in association with the production of a superoxide anion and other oxygen free radicals. Although long term effects of fetal exposure to environmental pollution level of PQ(II) and to its subclinical dose are not known, some studies on prenatal exposure to low level of PQ(II) have shown compelling evidence that PQ(II) can be transferred from the mother to the fetus, which compromise brain development and function in later life (Park, Kima, Kwon, Park, & Kima, 2010). Among the different techniques generally used for the measurement of PQ(II) concentrations include Chromatography HPLC (UV) or (GC) (Aramendıa et al., 2006; Grey, Nguyen, & Yang, 2002; Nunez, Kim, Moyano, Galceran, & Terabe, 2002; Posecion, Ostrea, & Bielawski, 2008), immunoassay (Niewola, Benner, & Swaine, 1986), potentiometry (Cosofret & Buck, 1984; Saad, Ariffin, & Saleh, 1998) and polarography (Walcarius & Lambers, 1996), molecules surface-enhanced Raman spectroscopy (MSERS) (Guerrini, Garcia-Ramos,

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Domingo, & Sanchez-Cortes, 2009), electrochemical methods (El Harmoudi et al., 2013), optical sensor (Mallat, Barzen, Abuknesha, Gauglitz, & Barcelo, 2001), spectrofluorimetry (Perez-Ruíz, Martínez-Lozano, Tomas, & Fenoll, 1998), spectrophotometry (Infante, Morales-Rubio, Guardia, & Rocha, 2008), enzyme-linked immunosorbent assay (ELISA) (Abuknesha & Luk, 2005; Spinks, Wang, Mills, Morgan, & Wang, 1999).

Electrochemical methods are also widely used as analytical technique that provides trace paraquat determination with height sensitivity and simplicity (Lívia, Luiz, Geiser, Orlando, & Craig, 2013; Xiaoliang, Yonge, & Chunming, 2012). Among of them, electrochemical impedance spectroscopy (EIS) is a technique which has been used for several decades (Randviir & Banks, 2013; Macdonald, 2006). It is one of the most informative techniques for the characterization of the electrochemical interface (Gebala & Schuhmann, 2012; Nam et al., 2013) providing a more complete analysis of the mechanism of action of the analyte; they allow the separation of the different mechanisms involved in the blocking process of electrode surfaces. However, the operation is more complex since it is sometimes difficult to find the best solution corresponding to the equivalent electrical circuit electrode interface/solution. One should bear in mind the high sensitivity of electrochemical impedance spectroscopy (EIS) methods, based on the adsorption exhibited by numerous organic compounds on some electrodes. EIS has proven to be efficient in the field of chemical analysis due to speed in the acquisition of the results, portability and good sensitivity (Xiulanb et al., 2011). The immunosensor bases on glassy carbon electrode modified with a composite made from fullerene, ferrocene and the ionic liquid was investigated by electrochemical impedance spectroscopy. It offers good repeatability, a stability, an impedimetric response to paraquat in the range from 3.89×10^{-11} to 4.0×10^{-8} mol L^{-1} and a detection limit of 9.0×10^{-12} mol L^{-1} (Xiulanb et al., 2011).

The object of this study was to establish a highly sensitive and stable electrochemical silver electrode for the detection of PQ(II). The paraquat tends to bind at silver surface by forming a stable paraquat/chloride/Ag complex (Kreisig, Tarazona, & Koglin, 1997). The evaluation of the protective power of a paraquat-complex, obtained at the silver electrode, was conducted by electrochemical impedance spectroscopy (EIS). The main parameters governing the impedance responses of paraquat were also optimized, including operating pH, potential and frequency of imposed potential.

2. Experimental

2.1. Instrument and reagent

All reagents used were of analytical grade or of the highest purity available. Sodium hydroxide, sulfuric acid, chloridric acid and ethanol were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies and were used as received. Solutions of paraquat (Sigma, St. Louis, MO, USA) were prepared by dissolving the herbicide, without further purification step. More diluted paraquat standards were obtained by dilution of this solution. The measurements were done *via* an electrochemical impedance analyzer potentiostat (model PGZ 100, Eco Chemie B.V, Utrecht, The Netherlands) with an electrochemical cell involving three electrodes: the working silver electrodes, a platinum counter electrode and a saturated electrode (3.00 mol L^{-1} AgCl). These measurements are carried out using a computer controlled by voltalab master 4 software logiciel. The working electrodes were constructed from 5 mm diameter silver wire which was inserted into glass tubing of approximately 10 mm internal diameter and insulated with Epoxy resin. After the drying of the resin, the electrodes were polished with a mechanical polisher and glass paper of different sizes and then cleaned with distilled water.

2.2. Analytical procedure

Electrochemical impedance measurements of paraquat were performed in 40 mL of an aqueous solution at pH 7.0. The impedance spectra were measured in the frequency range from 100 mHz to 100 kHz in a potential of 0.0 mV versus Ag/AgCl. The admittance *Y* was expressed in terms of a real (*Yr*) and imaginary (−*Yi*) component. Impedance signals were recorded after 3 min of reaction between the electrode and paraquat solution. The detection

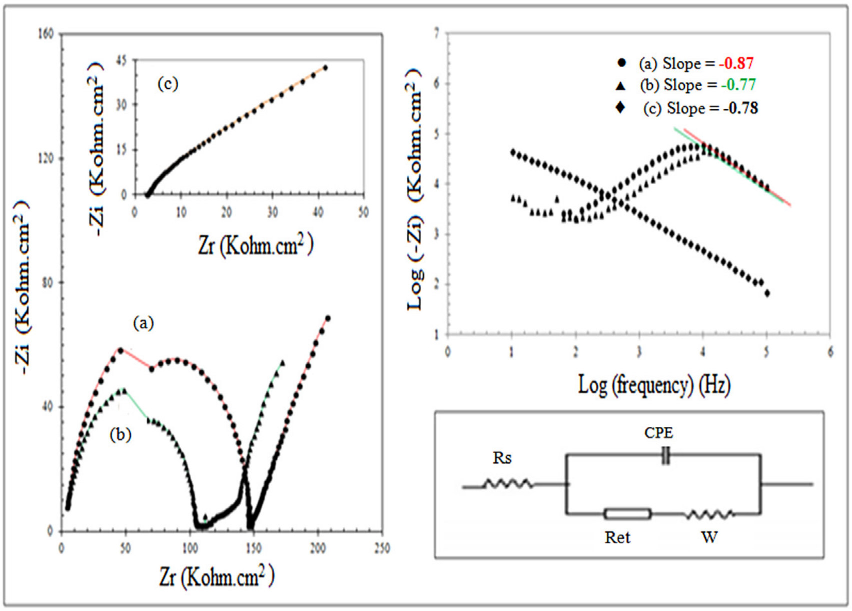

Fig. 1. Faradaic impedance spectra of silver electrode at different concentration of paraquat: (a) solution blank, (b) 1.0×10^{-11} mol L^{-1}, (c) 1.0×10^{-3} mol L^{-1}. Symbols represent the measured data, while solid line was the theoretical spectra of equivalent circuit. Insert: equivalent circuit. Variation of log (−*Zi*) versus log (frequency) of paraquat.