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ORIGINAL ARTICLE

# Silver particles-modified carbon paste electrodes for differential pulse voltammetric determination of paraquat in ambient water samples



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**Abstract** This paper describes the construction of silver particles-impregnated carbon paste electrode (Ag-CPE). The new electrode revealed an interesting determination of paraquat (II). The latter was accumulated on the modified electrode surface by adsorption onto silver particles and was reduced in 0.1 mol L<sup>-1</sup> of Na<sub>2</sub>SO<sub>4</sub> electrolyte at -0.70 V and -1.0 V for peaks 1 and 2, respectively. Experimental conditions were optimized by varying the heating temperature of the silver/carbon composite, the Ag/CP ratio, pH of measuring solution and accumulation time. Under the optimized working conditions, calibration graphs were linear for the concentration ranging from 1.0 × 10<sup>-7</sup> to 1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> with detection limits (DL, 3σ) 3.3 and 6.4 × 10<sup>-9</sup> mol L<sup>-1</sup>, respectively, for peaks 1 and 2. The precision of this methodology was evaluated for eight successive measurements of the same samples containing 1.0 × 10<sup>-4</sup> mol L<sup>-1</sup> of paraquat. The relative standard deviations (D.S.R.) were 1.9% and 2.4% for the peaks 1 and 2, respectively. The Ag/CP composite was characterized by X-ray diffraction (XRD) and BET adsorption analysis.

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## 1. Introduction

Paraquat (1,1-dimethyl-4,4-dipyridinium chloride) (PQ) is a quaternary nitrogen herbicide and an important tool for weed management, it controls many species and can be used with most crops. Paraquat is very fast-acting in all seasons and conditions (hot, dry, and wet), kills a wide range of annual grasses and broad-leaved weeds and then becomes inactive in the soil

allowing rapid turnaround and planting of another crop (Coasts et al., 2006). Using paraquat reduces soil erosion and competition among crops for space, water, light and nutrients. This means better quality, clean crops and higher yields. All these properties led to paraquat being used for the development of no-till farming (Huggins and Reganold, 2008). However, the major problem of paraquat is caused by his abusive and uncontrolled use which led to his high persistence in the environment. After it is slightly absorbed and binds quickly to the soil, paraquat easily leaches into water sources due to its high solubility (620 g L<sup>-1</sup> at 25 °C) (Halfon et al., 1996). Though its use is restricted in many countries, the occupa-

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tional, accidental, or intentional exposure of humans to paraquat still occurs (Madeley, 2002). For example, brain damages are found in patients, who drank paraquat solution (Hughes, 1988). In particular, several studies suggest a link between paraquat use and Parkinson's disease (PD) (Dinis-Oliveira et al., 2006). Biochemically, paraquat interferes with intracellular electron transfer systems in plants and animals leading to the formation of superoxide anion singlet oxygen as well as hydroxyl and peroxy radicals (Bus and Gibson, 1984). These reactive oxygen species (ROS) may interact with unsaturated lipids of membranes resulting in the destruction of cellular organelles and can lead to necrotic and apoptotic death (Suntres, 2002). Excessive ROS production has been implicated in male and female infertility and the pathophysiology of low-birth weight babies (Kim et al., 2005). Studies with frogs, birds and rodents suggest paraquat exposures, at environmentally relevant concentrations, elevate risks of declines in reproductive success due to embryotoxicity, delayed conception and malformations (Hausburg et al., 2005). Several analytical approaches have been applied for paraquat quantification, such as, chromatography CLHP (UV) or (CPG) (Zou et al., 2011; Norberto et al., 2008), immunoassay (Garcia-Febrero et al., 2014) and polarography (Walcarius and Lambers, 1996). The electrochemical determination of paraquat has been also performed at different electrode surfaces (Souza et al., 2006; Gustave et al., 2012). Various electrochemical techniques utilizing silver based electrode were used for the detection of a variety of organic and inorganic compounds (Bogusaw and Magorzata, 2008; Encarnación et al., 2007). These electrodes present a high capacity of adsorption and can therefore decrease the hydrogen discharge that can be explained by a blocking action of adsorbed compounds (Hepel and Osteryoung, 1983).

Herein, an electrochemical analysis of paraquat on carbon paste electrode modified with silver (Ag-CPE) was studied. The optimized electrode has a great ability to adsorb paraquat and provide an easy voltammetric quantitative analysis for some electro-active molecules. The electrochemical characterization and voltammetric performance of adsorbed electroactive paraquat were evaluated using differential pulse voltammetry.

## 2. Experimental

### 2.1. Reagents

All chemicals used were of analytical grade or of the highest purity available. Sodium sulfate, sodium hydroxide, silver nitrate and chloridric acid, were obtained from Merck, Fluka, and Riedel de Haen Chemical Companies and were used as received. Paraquat ions (Sigma, St. Louis, MO, USA) were dissolved in  $0.1 \text{ mol L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  to prepare stock solutions of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$ . Then the working standard solutions were prepared by successive dilution of the stock solutions by sodium sulfate. Carbon paste was supplied from Carbone, Lorraine, ref 9900, France. All other reagents used were of analytical grade. Distilled water (DW) was used throughout the preparation of the solutions.

### 2.2. Preparation of the Ag-CPE

The modified carbon paste electrodes were obtained by a mixture of silver nitrate ( $\text{AgNO}_3$ ) with a paste carbon (CP), for the

given  $\text{AgNO}_3/\text{CP}$  ratios 1%, 2%, 3%, 4%, 5%, 6%, 7%, 10%, 15% and 25% by weight (w/w). The  $\text{AgNO}_3/\text{CP}$  mixture was ground in an agate mortar and heated at the indicated time for 6 h in the kiln. The resulting mixture paste was then incorporated into the electrode cavity (laboratory made,  $0.1256 \text{ cm}^2$  geometric surface area) and was polished by smooth paper. Electrical contact was established by a bar of carbon. The resulting electrode is hereby denoted as Ag-CPE. The electrodes modified with  $\text{AgNO}_3$  and carbon paste alone (CPE) were prepared in a similar way.

### 2.3. Instrument

Electrochemical measurements were carried out by using an eDAQ e-corder/potentiostat EA163 controlled by eDAQ EChem data acquisition software and equipped with three-electrode system mounted on cell. The working (Ag) modified carbon paste electrode, the saturated calomel electrode ( $3.00 \text{ mol L}^{-1} \text{ AgCl}$ ) and a platinum electrode were used as reference and counter electrodes respectively. The pH-meter (Radiometer, SENSION™, PH31, 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), ( $K_{\text{Cu}} = 1.5406 \text{ nm}$ ) produced at 30 kV and 25 mA. The diffraction angles ( $2\theta$ ) were scanned between  $10^\circ$  and  $80^\circ$  with a step size of  $0.02^\circ 2\theta$  per second. The surface area was determined by the BET method (Autosorb iQ of Quantachrome instruments).

### 2.4. Procedure

The initial working procedure consisted of measuring the electrochemical response of Ag-CPE with a fixed concentration of paraquat. Standard solution of paraquat was added into the electrochemical cell containing 20 mL of supporting electrolyte  $0.1 \text{ mol L}^{-1}$  of  $\text{Na}_2\text{SO}_4$ . The mixture solution was kept quiet for 20 s for each electrochemical measurement. The differential pulse voltammetry was recorded in the range from  $-0.3$  to  $-1.4 \text{ V}$ , for which the scan rate is  $10 \text{ mV/s}$ , pulse height  $25 \text{ mV}$ , modulation amplitude  $5 \text{ mV}$ , frequency  $50 \text{ Hz}$  and scan increment  $50 \text{ ms}$ . Optimal conditions were established by measuring the peak currents which depend on all parameters. Under these conditions, suitability of the electroanalytical method in the determination of paraquat in underground water was tested. All experiments were carried out at room temperature and performed in triplicate.

## 3. Results and discussion

### 3.1. Preliminary voltammetric characterization

According to previous work (El Harmoudi et al., 2013), two peaks  $P_1$  and  $P_2$  were observed for the Ag-CPE electrode between  $-0.3$  and  $-1.2 \text{ V}$  due to  $\text{PQ}^{2+}/\text{PQ}^+$  and  $\text{PQ}^+/\text{PQ}^0$ , respectively. For comparative response of unmodified and modified carbon paste electrodes (CPE and Ag-CPE), a differential pulse voltammetry was used, since it is well recognized to be a more sensitive technique. Very sharp and well-defined peaks were obtained using Ag-CPE between  $-0.7$  and  $-1.0 \text{ V}$  (Fig. 1). Compared to CPE, Ag-CPE clearly showed a higher sensitivity of paraquat in terms of an enhanced current density.

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