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Analytical Methods

Square wave voltammetry for analytical determination of paraquat at carbon paste electrode modified with fluoroapatite

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ABSTRACT

This paper describes the construction of a carbon paste electrode (CPE) impregnated with fluoroapatite (FAP). The new electrode (FAP–CPE) was revealed an interesting determination of paraquat. The latter was accumulated on the surface of the modified electrode by adsorbing onto fluoroapatite and reduced in 0.1 mol L^{-1} K_2SO_4 electrolyte at -0.70 and -1.0 V for peaks 1 and 2, respectively. Experimental conditions were optimized by varying the accumulation time, FAP loading and measuring solution pH. Under the optimized working conditions, calibration graphs were linear in the concentration ranging from 5×10^{-8} to 7×10^{-5} mol L^{-1} with detection limits (DL, 3σ) of 3.5×10^{-9} and 7.4×10^{-9} mol L^{-1}, respectively, for peaks 1 and 2.

Fluoroapatite was characterized by X-ray diffraction XRD analysis; Fourier-transform infrared spectroscopy FT-IR and inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis.

1. Introduction

The wide use of pesticides and herbicides in agriculture to preserve crops from pests, as well as their high intrinsic toxicity, associated, in many cases, with a remarkable persistence in the environment, represent a potential danger for the health of ecosystems. The control of their concentration in different matrices is a key component of any environmental control. A wide number of analytical methods, based on the most commonly employed physico-chemical techniques for the identification of organic compounds are used: High-performance liquid chromatography (HPLC) and gas chromatography (MacDonald & Meyer, 1998), HPLC, UV (Baskaran, Kookana, & Naidu, 1997; Berny, Buronfosse, Videmann, & Buronfosse, 1999; Navalon, El-Khattabi, Gonzalez-Casado, & Vilchez, 1999; Macke et al., 1999; Martynez-Galera, Garrido Frenish, Martynez-Vidal, & Parrilla-Vazquez, 1998; Vilchez, El-Khattabi, Blanc, & Navalon, 1998) or amperometric detection (Fernandez-Alba, Valverde, Agura, Contreras, & Chiron, 1996) and Fluorimetric method (Vilchez, El-Khattabi, Blanc, & Navalon, 1998). Stripping analysis is an extremely sensitive electrochemical technique for measuring trace level electroactive organic compounds (Zuman, 2000). The use of modified electrodes in selectively preconcentrating organic analytes is also attracting interest (Manisankar, Selvanathan, Viswanathan, & Prabu, 2002; Manisankar, Viswanathan, & Prabu, 2002; Manisankar, Viswanathan, & Prabu, 2004). It provides a highly sensitive route to the measurement of many electroactive organic compounds (Guiberteau, Galeano, Mora, Parrilla, & Salinas, 2001; Manisankar & Prabu, 1995; Garrido, Costa lima, Delerue-metos, Borges, & Oliveria Brett, 2001; Hernandez, Palchetti, & Masscini, 2000; Ibrahim, Almagboul, & Kamal, 2001; Oudou, Alonso, & Jemenez, 2001; Sreedhar, Samatha, & Sujatha, 2000; Zen, Kumar, & Chang, 2000).

Paraquat (PQ) (1,1′-dimethyl-4,4′-bipyridylium chloride), is one of the bipyridinium compounds (Bromilow, 2000) which was extensively used as a non-selective herbicide. However, it is well known that this compound is also one of the most acutely toxic compounds because it has caused many cases of human poisoning, with the lung being the primary target tissue (Chen & Lua, 2000).

It was previously shown that Lu and Sun (2000) used a nafion modified glass carbon electrode for the analytical determination of paraquat employing differential pulse voltammetry as an analytical technique. Souza, Machado, and Pires (2006) applied multiple square wave voltammetry for the analytical determination of paraquat in natural water, food, and beverages using microelectrodes, reaching a determination limit as low as 7.1 ppb. Walcarius, Lamberts, and Deroune (1993) studied the electrochemical behavior of paraquat at carbon paste electrodes modified by zeolites, using cyclic voltammetry, chronoamperometry, square wave voltammetry and chronocoulometry. The development of chemical sensors

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components has promoted recent innovations in the electroanalytical determination, generating new possibilities in order to increase the signal peaks and to lower detectable concentration of paraquat in different samples, using different electrodes surfaces.

The purpose of this paper is to study the applicability of carbon paste electrode (CPE) modified by fluoroapatite (FAP) using square wave voltammetry (SWV) for the electroanalytical determination of paraquat. The modifier (FAP) of carbon paste is a common source of phosphates, particularly in the Moroccan natural phosphates because it is the most stable and insoluble of all the calcium phosphates. It occurs in a wide range of substituted forms, both biological and mineralogical (Montel, Bonel, Trombe, Heughebaert, & Rey, 1977).

To attest the applicability of the proposed methodology, the effect of interference was evaluated using natural water samples taken from river OUM ER RBIA situated in Tadla-Azilal region, Morocco. The aforedescribed methodology was also applied to potato and apple samples. All samples were used directly for experiments, without pretreatment or separation step. These experiments were performed to evaluate the matrix interference effect in the application of the methodology in complex samples.

2. Experimental

2.1. Apparatus

All electrochemical experiments were performed with a potentiostat (model PGSTAT 100, Eco Chemie B.V., The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The tree-electrode system consisted of a modified carbon paste working electrode, a SCE reference electrode and a platinum plate auxiliary electrode. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

X-ray diffraction studies of prepared powder were carried out using a diffractometer (XRD: Cu Kα radiation, Philips XPERT MPD), ($\lambda = 1.5406$ nm) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 10° and 70° with a step size of 0.02° 2θ per second. From X-ray diffraction data, the lattice parameters a and c were found using the least-squares method (AF-part program). The volume V of the hexagonal unit cell was determined for HAP formulation from the relation $V = a^2 \times c \times \sin 2\pi/3$.

Fourier transformed infrared spectroscopy (FTIR) analysis (Perkin–Elmer FTIR) was performed in order to determine fluorapatite stoichiometry deviations, in particular the PO_4^{3-} groups. In order to evaluate Ca/P ratio of the powder, inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed.

2.2. Reagents

Carbon paste was supplied from (Carbone, Lorraine, ref 9900, French). Potassium sulfate, calcium nitrate, and diammonium phosphate were purchased from Fluka. Paraquat was purchased from (Sigma, St. Louis, MO, USA). Working standards for calibration were prepared by diluting the primary stock solution with doubly distilled water (BDW). All chemicals were of analytical grade and used without further purification.

2.3. Preparation of FAP

The synthesis of fluorapatite is carried out by reaction between diammonium phosphate and calcium nitrate in presence of ammonia. An amount of 250 mL of a solution containing 7.92 g of diammonium phosphate, maintained at a pH greater than 12 by addition of ammonium fluoride (70 mL), was dropped under constant stirring into 150 mL of a solution containing 23.6 g of calcium nitrate ($Ca(NO_3)_2 \cdot H_2O$). The pH of the mixed solution was maintained at 10 by the addition of concentrated ammonium fluoride (NH_4F) solution. After the completion of addition, the reaction was performed at 90 °C for 3 h under a constant stirring condition. The suspension was refluxed for 4 h. The obtained fluorapatite was filtered, washed with BDW, dried overnight at 80 °C and calcined at 900 °C for 3 h before use.

2.4. Construction of FAP–CPE

The graphite powder and fluoroapatite were hand-mixed in different ratios (w_{FAP}/w_{CP}) by weight. A certain quantity of the mixture was packed firmly into the cavity (geometric area 0.1256 cm^2) of PTFE cylindrical tube electrode of a plastic pipette tip. Electrical contact was established with a bar of carbon. The resulting electrode is hereby denoted as FAP–CPE. The electrodes modified with the FAP (FAP–CPE) and carbon paste alone (CPE) were prepared in a similar way.

2.5. Procedure

For the preconcentration step, the modified CPE was briefly rinsed with BDW and immersed in a stirred 20 mL of 0.1 mol L^{-1} K_2SO_4 containing a known amount of paraquat solution at open circuit. Then, cyclic and square wave voltammetric experiments were performed after purging the solutions for 10 min with pure nitrogen. For cyclic voltammetry the potential range was from -0.3 to -1.3 V at scan rate of 50 mV s^{-1}. SWV scanning was performed from -0.3 to -1.2 V with a step potential 25 mV, amplitude 5 mV and duration 5 s at scan rate 1 mV s^{-1}. All measurements were carried out at room temperature.

For the square wave voltammetric determination of paraquat ions in potato and apple samples, 20 mL of a fresh sample was transferred into the voltammetric cell. Meanwhile the solution was stirred by a 1.6 cm magnetic strirrer bar (rotating about 600 rpm) at open circuit.

3. Results and discussion

3.1. Characterization of the prepared powder

The XRD pattern of the prepared powder was presented in Fig. 1. After calcination of the powder at 900 °C for 3 h, the pattern obtained from the XRD traces were a good match to the pattern for phase pure fluoroapatite [JCPDS pattern 09-0432]. It should be noted that X-ray diffraction analysis of precipitated apatite powder resulted in diffraction pattern that could resemble that of FAP. Based on the chemical analysis, the amount of calcium (Ca), phosphorus (P), and fluorine (F) found resulted in a Ca/P ratio of 1.67 and % F of 3.7%, which are in agreement with the stoichiometric values of FAP. This justifies the purity of samples and the suitability of the method adopted for synthesis with the operator conditions used as well as for chemical analysis. X-ray patterns of the samples reveal the existence of a single phase and are indexed on the basis of the hexagonal system (space group $P63/m$). The crystallographic lattice parameters calculated using the AF-part program were $a = 9.364 \pm 0.003$ Å, $c = 6.893 \pm 0.003$ Å and $V = 520$ Å^3. FT-IR spectra displayed in Fig. 2 also confirm the formation of apatite phases for synthesis powder with the observed fundamental vibrational modes of PO_4^{3-} group at 475, 574, 609, 966 and 1020–1120 cm^{-1}. No spectral bands corresponding to carbonates ions were noted.

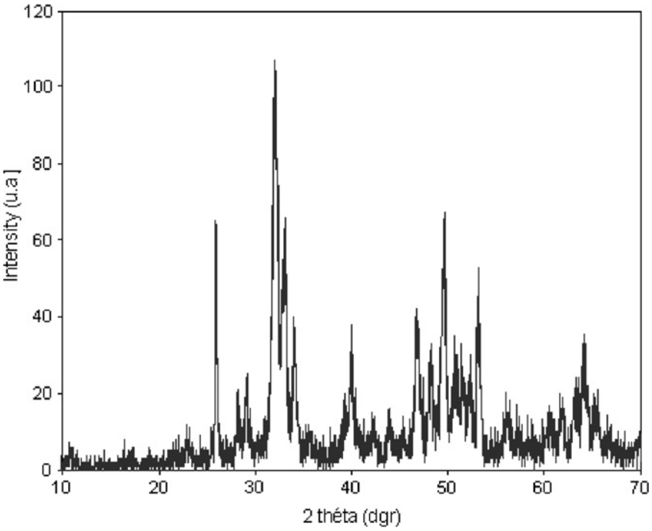

Fig. 1. XRD patterns fluoroapatite heated at 900 °C for 3 h.

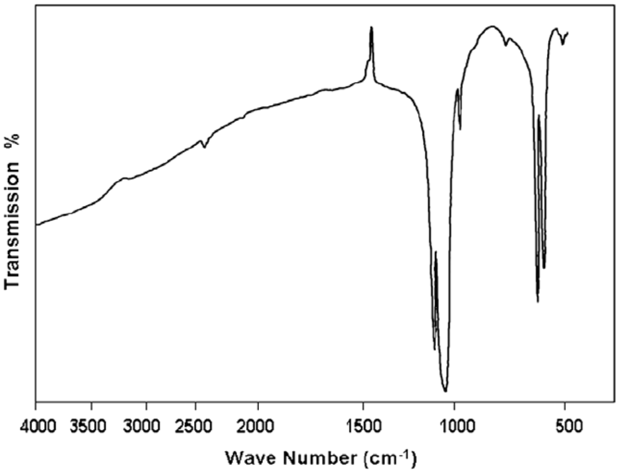

Fig. 2. IR spectra of the apatite calcined at 900 °C for 3 h.

3.2. Voltammetric behavior of paraquat on FAP modified CPEs

Several analyses were performed in order to evaluate the modifier electrodes proposed here. The cyclic voltammogram of the FAP–CPE recorded in blank K_2SO_4 (0.1 M, pH 8.0) solution is reported. With paraquat it was found that two pair peaks appeared (P_1,P_4) and (P_2,P_3) at fluoroapatite modified carbon paste electrode. This is attributed respectively to PQ^{2+}/PQ^{+} and PQ^{+}/PQ^{0} redox couple. These illustrations are consistent with those described elsewhere for paraquat (Lu & Sun, 2000; Souza & Machado, 2005). Comparing FAP–CPE with CPE, voltammogram enregistred at FAP–CPE shows a distinct couple of waves; it seems that there was some degree of reversibility of the redox processes. The cyclic voltammetric curves recorded for paraquat exhibit a reversible charge transfer for the reduction of the pyridinium cations (P_1 and P_2). After the second electron transfer to the pyridinium cations, the electronic density remains localised on the neutral ring. Peaks 1 and 2 can thus be associated, respectively, to the redox couple (1) and (2) (Elofson & Edsberg, 1957):

$$\text{Paraquat(II)} + e^- \rightarrow \text{Paraquat(I)} \qquad (1)$$

$$\text{Paraquat(I)} + e^- \rightarrow \text{Paraquat(0)} \qquad (2)$$

In this paper the catodic response of paraquat was systematically studied using square wave voltammetry at freshly prepared unmodified and modified CPEs in 0.1 mol L^{-1} K_2SO_4 solution. However, at unmodified electrode surface, the peaks currents are smaller than that at the modified electrode. The performance of the newly developed fluoroapatite modified carbon paste electrode is based on the preconcentration of paraquat from aqueous solution onto the surface of the modified electrode by fixation with the modifier. By this means, the sensitivity of the determination of paraquat is greatly increased.

3.3. Optimization of experimental conditions

The accumulation of paraquat at the FAP modified CPE was based on the adsorption process of paraquat onto modifier surface. Therefore, the percentage of FAP in the carbon paste had a significant influence on the voltammetric response. Six different modified carbon pastes (12.5%, 25%, 37.5%, 50%, 62.5% and 75% by weight) were tested for their voltammetric signals. Maximum current was obtained when the fluoroapatite composition in the paste was 37.5%. Higher concentrations of FAP decreased the peak current significantly. This is presumably due to the reduction of conductive area (carbon particles) at the electrode surface. In fluoroapatite, the conduction mechanism is related to the translational hopping of fluoride ions along the *c* axis of the unit cell from ordinary lattice sites in interstitial sites and back again, which are the only candidates for such a conduction process. The fluoride ions must be able to move to other positions by the formation of thermally activated defects such as Schottky defects with high activation energies, because the fluoroapatite materials are stoichiometric (Laghzizil, El Herch, Bouhaouss, Lorente, & Macquete, 2001). Hence an electrode containing 37.5% FAP was employed in all subsequent experiments.

For constant paraquat concentration, i.e. 5×10^{-7} mol L^{-1}, the dependence of cyclic voltammetric peak current on the preconcentration time was studied at FAP–CPE (3:5) in 0.1 M K_2SO_4 at pH 8.0. The peak current increases with the increase of the preconcentration time, indicating an enhancement of paraquat ion concentration at the surface of the electrode, when a preconcentration time is equal to 15 min, the peak current becomes constant. Hence for all subsequent measurements, a preconcentration time (t_p) of 15 min was employed.

The effect of varying pH on the current response of FAP–CPE at constant paraquat concentration (4.27×10^{-5} M) was performed under these selected conditions. The current response increased from the pH 2.0 until pH 5.5, where it stabilized until pH 9.0, but then, it decreased. As mentioned earlier, paraquat is preconcentrated onto FAP–CPE at open circuit potential. It is known that in acidic solution, there are more proton ions competing with paraquat on the adsorption onto fluoroapatite. The peak potentials do not, however, seem to be affected by the concentration of H^+, suggesting the absence of any protonation step in the reduction mechanism. The preconcentration efficiency of fluoroapatite for paraquat is lower in acidic solutions than in basic solutions.

3.4. Calibration graph

The square wave voltammetric peaks current was measured, using the set of optimum conditions, for a series of paraquat concentrations ranging from 5×10^{-8} to 71.25×10^{-6} mol L^{-1} (Fig. 3), the response was linear with 15 min accumulation time. The flowing equations were $Ip_1 = 1.765 \times 10^{-6}$ [paraquat] + 16.814 and $Ip_2 = 1.287 \times 10^{-6}$ [paraquat] + 8.673 (where *I* is expressed in μA cm^{-2} and [paraquat] in mol L^{-1}). The linear correlation coefficients are 0.982 (P_1) and 0.991 (P_2). The detection limits (DL, 3σ) are 3.5×10^{-9} mol L^{-1} and 7.4×10^{-9} mol L^{-1} for peaks 1 and 2,

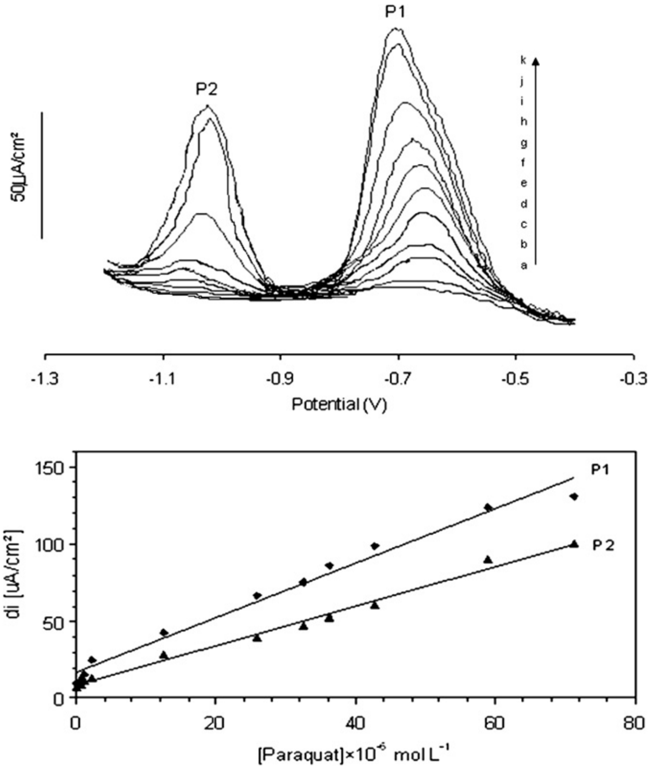

Fig. 3. Square wave voltammograms at FAP–CP electrode with FAP:CP = (3:5) and 15 min of precencentration time in 0.1 mol L^{-1} K_2SO_4 (pH 8.0) for different concentrations of paraquat: (a) 5×10^{-8} mol L^{-1}; (b) 7×10^{-7} mol L^{-1}; (c) 1.2×10^{-6} mol L^{-1}; (d) 2.3×10^{-6} mol L^{-1}; (e) 12.6×10^{-6} mol L^{-1}; (f) 25.9×10^{-6} mol L^{-1}; (g) 32.5×10^{-6} mol L^{-1}; (h) 36.25×10^{-6} mol L^{-1}; (i) 42.75×10^{-6} mol L^{-1}; (j) 58.9×10^{-6} mol L^{-1} and (k) 71.25×10^{-6} mol L^{-1}.

respectively, and the quantification limits (QL, 10σ) are 1.16×10^{-8} mol L^{-1} and 2.46×10^{-8} mol L^{-1} for peaks 1 and 2, respectively. The measurements of 5×10^{-8} mol L^{-1} of paraquat was carried out seven times at different electrodes. The relative standard deviation (RSD) was 1.4% and 1.8%, respectively, for peaks 1 and 2. The results indicate that the FAP–CPE has excellent reproducibility. The results obtained here show that the proposed SWV method is fast, sensitive and better suited than conventional methods, like spectrophotometry or chromatography (Ibanez, Pico, & Manes, 1996; Rai, Das, & Gupta, 1997), to characterizing fast variations in concentration of dilute paraquat aqueous solutions. Most of these techniques are either suffer from the instability of the reagent and the instrumental system or require extensive sample pretreatment. Additionally, from careful analysis of the results obtained for the detection and quantification limits it is apparent that use of the FAP–CPE provides an alternative method for electrochemical detection of paraquat, with possibility of its employment for analytical determination of others pesticides that are frequently determined at mercury electrodes, which have the inconvenience of being highly toxic, or enzyme-based biosensors, which present difficulties involving costs and time in the realization of the analysis. In other hand, the DL and QL values obtained by the proposed procedure are lower than the maximum value permitted by the world organization of health, which is 70 µg L^{-1} (OMS, 1983), indicates that the method could be employed to analyze paraquat in realistic samples.

3.5. Practical application

The analytical utility of this procedure was assessed by applying it to the determination of paraquat in realistic samples containing this herbicide. The latter is extensively used in many countries as crop resistant against bad aquatic herbs, bad herbs in cultures and orchards, as desiccant and defoliant of cotton and potato, and as material of help to the harvest of the soya. However, these products represent a potential risk to humans, animals and environment because they have caused many cases of human poisoning, with the lung being the primary target tissue. This is the major reason why residue determination in foodstuffs is of such great interest.

In Morocco, the paraquat is one of the most widely used herbicides in potato and apple cultures. Due to its permitted use in such cultures, the methodology proposed was applied in order to evaluate the occurrence of matrix effects in the electroanalytical determination of paraquat residues directly in the samples, without pretreatment or clean up steps.

Twenty grams of apple and potato were transferred into an electrochemical cell, mixed and homogenized. The samples were used as received in preparing the supporting electrolyte (adding 0.1 mol L^{-1} K_2SO_4) and the analytical curves were again obtained by SWV experiments. No paraquat was detected in these two original samples so they were spiked with appropriate amounts of paraquat and were adjusted to a pH 8.0 value. The analytical sensitivities, defined by the slope of the analytical curves, were compared with that obtained with purified water, where it is possible to observe that the peak current values for the paraquat reduction process displayed some influence from the components of the samples employed, characterized by a decrease in the slope of the curves obtained. It was found that peaks currents iP_1 and iP_2 versus paraquat added into real samples increased linearly. These results indicate that the proposed methodology is suitable for the determination of paraquat in these samples. As summarized in Table 1 for spiked samples, the analytical response of analyte in voltammetric determination was slightly decreased compared to those obtained in pure electrolyte.

In square wave voltammetry, the background currents were intense and not really flat in potato and apple (Fig. 4), very likely due to the presence of electroactive interferences coming from the two samples, resulting probably from starch and sucrose in potato and apple respectively, which can inhibit the adsorption process of paraquat onto fluoroapatite surfaces. The decrease in the values of the slopes of the analytical curves reflects an electrochemical process involving adsorption of reagents and/or products, which can be inhibited by the presence of other components in the samples used.

The current response of paraquat in K_2SO_4 pure was measured as I_1. When the potato or apple was used, the current response was measured as I_2.

Samples were spiked with 2×10^{-5} mol L^{-1} of paraquat and the percentage of signal (I %) was calculated using Eq. (3). The results obtained were related to the interference effects of the constituents of each sample.

$$I\% = I_2/I_1 \times 100 \qquad (3)$$

The results of relative standard deviations and percentage signal that were obtained for peak 1 and peak 2, were considered satisfactory compared to those obtained using other analytical methods

Table 1
Results obtained from the linear regression curves for the determination of paraquat at FAP–CPE in natural samples under the optimal conditions

Parameters	Peak 1	Peak 2
R^2	0.9841	0.9823
Slope (A/mol L^{-1})	0.4153	0.2297
Standard deviation × 10^{-10} (A)	28.30	37.71
Relative standard deviation (%)	2.16	2.70

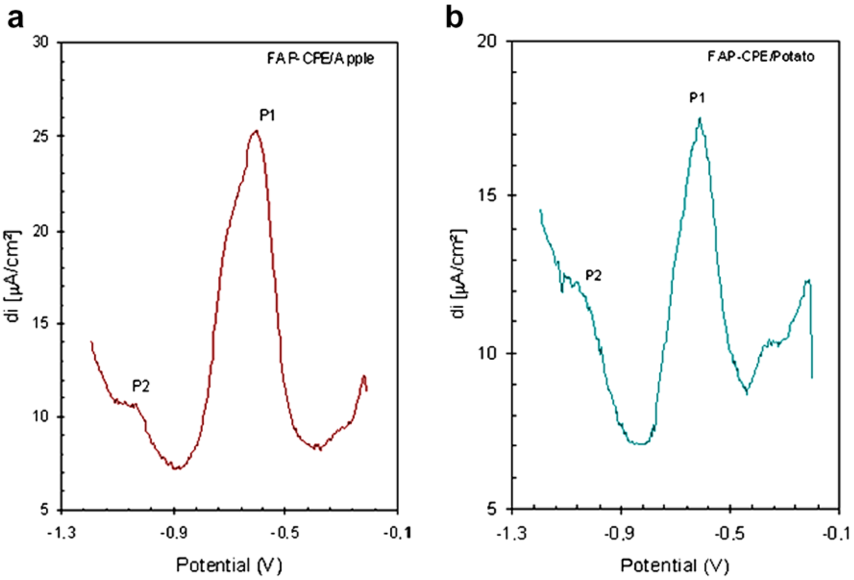

Fig. 4. Square wave voltammograms of 2.45×10^{-6} mol L^{-1} of paraquat at FAP–CPE in 0.1 mol L^{-1} K_2SO_4 containing (a) apple and (b) potato under the optimized conditions.

(Walcarius & Lambert, 1996). The proposed methodology has therefore proven to be applicable for use in complex samples.

4. Conclusion

In the present work, the primary goal, on using FAP–CPE, was to verify the possibility of obtaining responses of paraquat on cyclic and square wave voltammetry. The proposed FAP–CP electrode is a suitable electrochemical device for paraquat detection. Analytical results show that the proposed modified electrode was able to detect 3.5×10^{-9} mol L^{-1} of paraquat with good sensitivity and reproducibility. Additionally, the proposed methodology was successfully applied in determining paraquat in natural samples.

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