أقطاب من عجينة كربونية معدلة برقائق من الفضة لتعيين الباراكوات بطريقة النبض التفاضلي الفولتائي في عينات ماء عند حرارة الغرفة السائدة

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الملخص:

تصف هذه الدراسة بناء قطب من عجينة كربونية مشربة برقائق الفضة (Ag–CPE). بفضل هذا القطب الجديد أمكن تعيين المبيد الحشري باراكوات–2. وقد تراكم هذا المبيد على سطح هذا القطب المعدل بإمتزازه على رقائق معدن الفضة وتم اختزاله في وسط من محلول كبريتات الصوديوم (0.1 مول/ليتر) عند 0.07 و 1.0 فولت للقمم 1 و 2، على التوالي. لقد تم التحكم في ظروف التجربة للحصول على النتائج المثلى وذلك بتغيير كل من درجة تسخين القطب، نسبة الفضة الى عجينة الكربون، الأس الهيدروجيني للمحلول و مدة الإمتزاز. تحـــــت هذه الظروف المثلي للتجربة تم الحصول على منحنيات ارتباط خطية للتراكيز من 1×10^{-7} مول/ليتر إلى 1×10^{-3} مول/ليتر وبحدود تعيين لـ (DL,3σ) تساوي 3.3 و 1×10^{-4} مول/ليتر، على التوالي للقمم 1 و 2.

تم تقييم ضبطية هذه الطريقة لعدد ثمانية قراءات متتالية لنفس العينة التي احتوت على 1×10^{-4} مول/ليتر. من الباراكوات. وكانت الانحرافات المعيارية النسبية 1.9% و 2.4% للقمم 1 و 2 على التوالي. لقد تم تشخيص مؤلف الفضة/عجينة الكربون بواسطة حيود الأشعة السينية وتحليل امتصاص بروناوير–ايميت–تيلر (BET).

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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^{-1} of Na_2SO_4 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^{-7} to 1.0×10^{-3} mol L^{-1} with detection limits (DL, 3σ) 3.3 and 6.4×10^{-9} mol L^{-1}, 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^{-4} mol L^{-1} 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^{-1} at 25 °C) (Halfon et al., 1996). Though its use is restricted in many countries, the occupa-

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 peroxyl 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 mol L^{-1} of Na_2SO_4 to prepare stock solutions of 1.0×10^{-3} 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 ($AgNO_3$) with a paste carbon (CP), for the given $AgNO_3$/CP ratios 1%, 2%, 3%, 4%, 5%, 6%, 7%, 10%, 15% and 25% by weight (w/w). The $AgNO_3$/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 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 $AgNO_3$ 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 mol L^{-1} 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), (Kcu = 1.5406 nm) produced at 30 kV and 25 mA The diffraction angles (2θ) were scanned between 10° and 80° with a step size of 0.02° 2θ 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 mol L^{-1} of Na_2SO_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 V, for which the scan rate is 10 mV/s, pulse height 25 mV, modulation amplitude 5 mV, frequency 50 Hz and scan increment 50 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 V due to PQ^{2+}/PQ^+ and PQ^+/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 V (Fig. 1). Compared to CPE, Ag-CPE clearly showed a higher sensitivity of paraquat in terms of an enhanced current density.
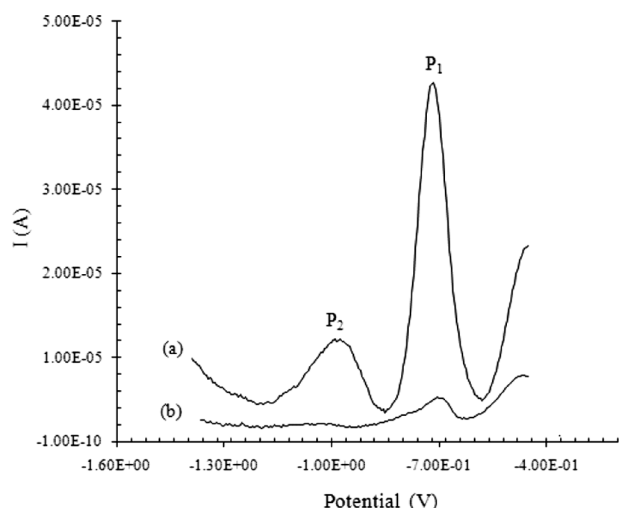
Figure 1 Differential pulse voltammograms of 1.0×10^{-4}-mol L^{-1} paraquat in 0.1 mol L^{-1} Na$_2$SO$_4$ (a) (Ag) modified carbon paste electrode (5% of AgNO$_3$/CP ratio heated at 200 °C), (b) carbon paste electrode heated at 200 °C, pH = 7.5.

3.2. Optimization of experimental conditions

3.2.1. Differential pulse parameters

The influence of the electrochemical experimental variables (frequency, pulse height, modulation amplitude and scan increment) involved in the differential pulse voltamme-try (DPV) determination of PQ(II) was investigated (Fig. 2). Measurements of electrolytic solution containing 1.0×10^{-4} mol L^{-1} of paraquat were performed for evaluating the heights and the shapes of the signals obtained.

The effect of frequency (v) on the current intensity (Ip) of paraquat using Ag-CPE was evaluated in the range from 5 to 50 Hz. The signal increased up to 50 Hz. Nevertheless, the maximum acceptable value in DPV program, which is 50 Hz and which corresponds to 0.02 s of duration for each step, was used in the present experimental study. The current peak was directly proportional to the frequency (v), indicating that this redox process is a reaction that involves adsorption as the rate-determining step (Lovric and Komorsky-Lovric, 1988). This behavior is typical of the responses obtained at electrodes, where the electroactive species interact with working electrode, in the adsorption process, before the redox reaction occurs.

Pulse height was studied in the range from 10 to 35 mV. The stripping signal underwent an increase of 72% up to 25 mV, where the highest peak intensity was obtained. A slight decrease in the signal was observed for higher values of pulse height. The amplitude influence was investigated in the range from 1 to 15 mV. The results obtained demonstrated that a height of the paraquat peak increased linearly as a consequence of the increase in amplitude values up to 5 mV. For higher value, the paraquat signal has remained stable due to peak broadening and the signal noise increased.
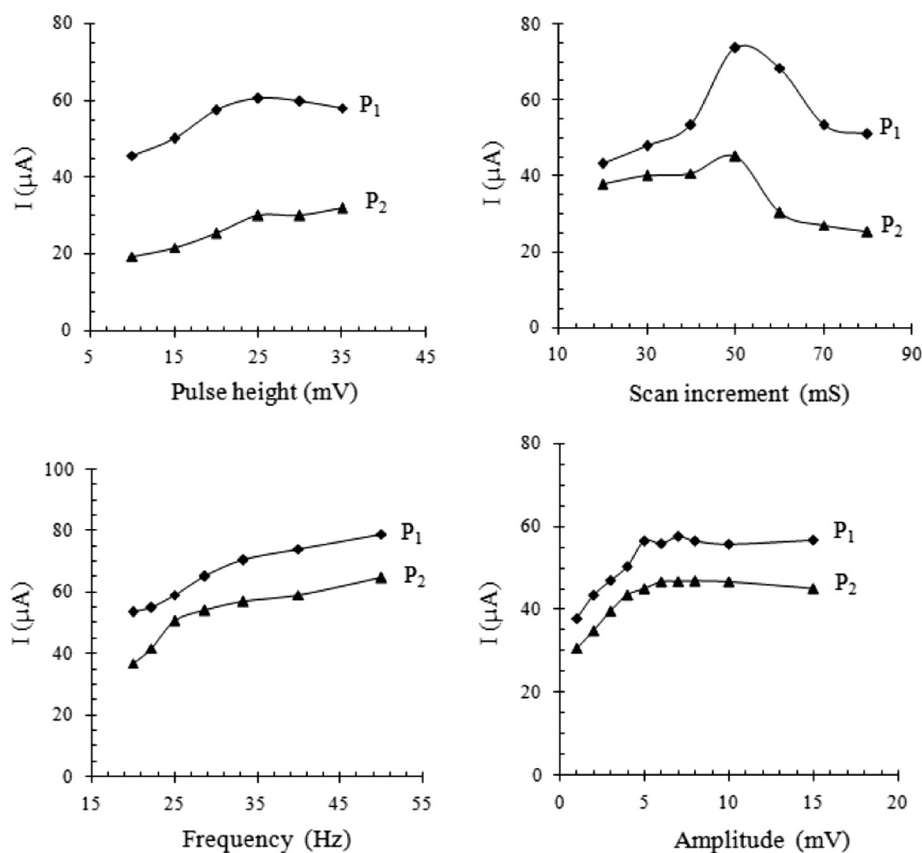

Figure 2 Influence of the experimental variables (pulse height, scan increment ΔEs, frequency, modulation amplitude) on differential pulse reduction peaks of 1.0×10^{-4} mol L^{-1} paraquat in 0.1 mol L^{-1} Na$_2$SO$_4$ at Ag-CPE, (AgNO$_3$)/CP = 5%.
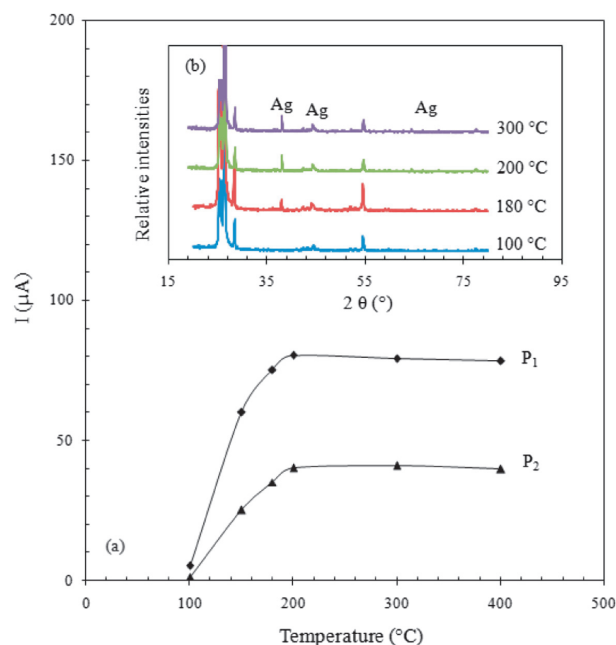
Figure 3 (a) Effect of heated temperature of AgNO$_3$/CP on differential pulse reduction peaks of 1.0×10^{-4} mol L^{-1} paraquat at Ag-CPE, (AgNO$_3$)/CP = 5%. (b) The XRD patterns of the (AgNO$_3$)/CP at different temperatures (100, 180, 200 and 300 °C), ratio of AgNO$_3$/CP = 5%.
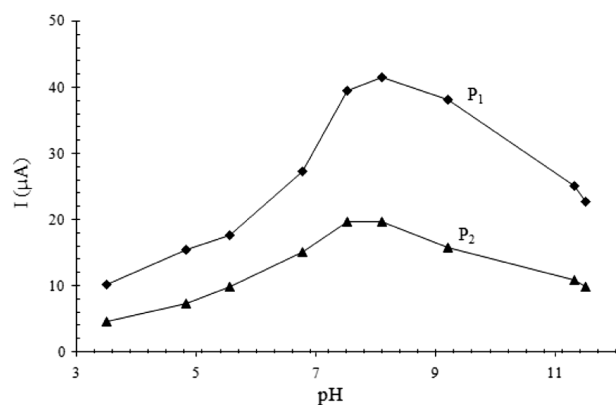
Figure 4 Effect of pH on differential pulse reduction peaks of 1.0×10^{-4} mol L^{-1} paraquat at Ag–CPE, (AgNO$_3$)/CP = 5%.

Using the optimized parameter values, the influence of increasing scan increment ΔEs on the current peak was tested in the range from 20 to 80 ms. As shown in Fig. 2, the height of the paraquat peak increased with ΔEs, up to 50 ms. The longer scan increment resulted in a decrease in intensity (Ip), indicated an adsorption process as the rate-determining step. In agreement with the high peak current values, good shapes of the signal and better signal to noise ratio, the selected optimal values were 50 Hz, 25 mV, 5 mV and 50 ms for frequency, pulse height, modulation amplitude and scan increment respectively.

3.2.2. Chemical parameters

For constant paraquat concentration 1.0×10^{-4} mol L^{-1}, the effect of heating temperature of carbon paste modified with

AgNO$_3$ (Ag/CP) on the differential pulse voltammetry response (Fig. 3a) was studied. The maximum response was observed for the AgNO$_3$/CP heated at 200 °C, 300 °C and 400 °C. XRD was carried out to explain the effect of heating temperature of the carbon modified with silver on DPV measurements. The characteristic peaks for Ag/CP powders, heated at 200 and 300 °C, were observed at 2θ 38.2, 64.5 due to {1 1 1} and {2 0 0} polycrystalline silver planes, respectively, with a great increase in intensity at these temperatures compared to the other temperature (Fig. 3b). For the sample heated to 100 °C, the absence of the metallic silver peaks was observed (Rameshbabu et al., 2007). This absence can be attributed to intense carbon peak observed at 2θ 26.17 which might be responsible for obscuring differentiation between the intensity of silver metallic peaks of samples. According to XRD analysis at 200 °C, 300 °C and 400 °C, the same intensity of silver metallic was observed. Hence, for all subsequent measurements, a mixture of the AgNO$_3$/CP heated to 200 °C was employed.

The effect of pH on the differential pulse voltammetry response of the Ag-CPE at pH ranging between 3.0 and 12.0 in 1.0×10^{-4} mol L^{-1} of paraquat is shown in Fig. 4. The optimum pH range was found between 7.5 and 8.5, showing a maximum response at pH 8.0. The sensitivity decrease in acidic solution was accompanied with the decrease in reduction peaks. This result is comparable to that found in published works (El Harmoudi et al., 2013). 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. A great effort has been devoted to the study of paraquat and their radical cations in the adsorbed state (Kreisig et al., 1997). The paraquat (II) can be reduced through a one-electron transfer step to the methyl viologen radical cation (PQ^{2+} + 1 e$^-$ ↔ PQ$^{\cdot +}$), which can reversibly form a dimer (Alden et al., 1997). The further monoelectronic reduction of PQ$^{\cdot +}$ to the fully reduced state, PQ^0 (PQ$^{\cdot +}$ + 1 e$^-$ ↔ PQ^0), occurs at more negative potentials and is less reversible because of the conproportionation reaction between PQ^0 and PQ^{2+} to generate 2PQ$^{\cdot +}$ (PQ^{2+} + PQ^0 → 2 PQ$^{\cdot +}$), which leads to adsorption on the electrode surface. This result is confirmed by Kreisig et al. (1997) using a Surface-enhanced Raman microprobe spectroscopy (micro-SERS), which allows rapid scanning over the surface of silver electrode and can therefore determine different adsorption sites on the silver surface.

The effect of the preconcentration time on the differential pulse voltammetry measurements was studied with Ag-CPE in 1.0×10^{-4} mol L^{-1} of paraquat (Fig. 5). The current intensity increased suddenly to reach a maximum at 8 min of accumulation time. Normally, the increase in the response current continued until the maximum signal level (presumably corresponding to either saturation or an equilibrium surface coverage) is attained. Hence, in all subsequent experiments 8 min preconcentration time was employed.

The accumulation of paraquat using Ag-CPE was based on the adsorption process of paraquat onto modifier surface. Therefore, the percentage of silver in the carbon paste had a significant influence on the voltammetry response. Different carbon pastes modified with silver were tested for their differential pulse voltammetry signals. Maximum current was obtained when the silver nitrate composition in the paste was 5% (Fig. 6a). To explain the effect of AgNO$_3$ percentage on
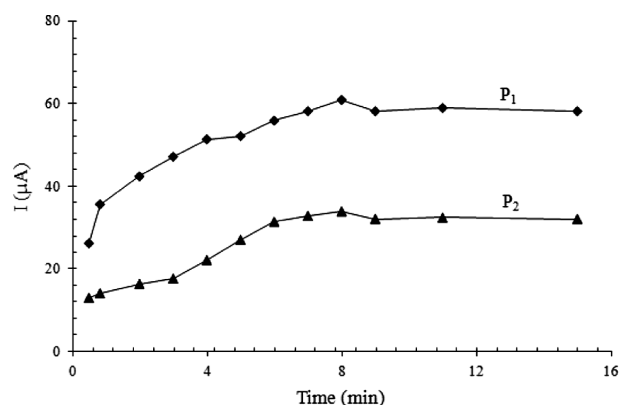
Figure 5 Influence of preconcentration time on differential pulse of 1.0×10^{-4} mol L^{-1} paraquat, pH = 7.8, (AgNO$_3$)/CP = 5%, at Ag-CPE.
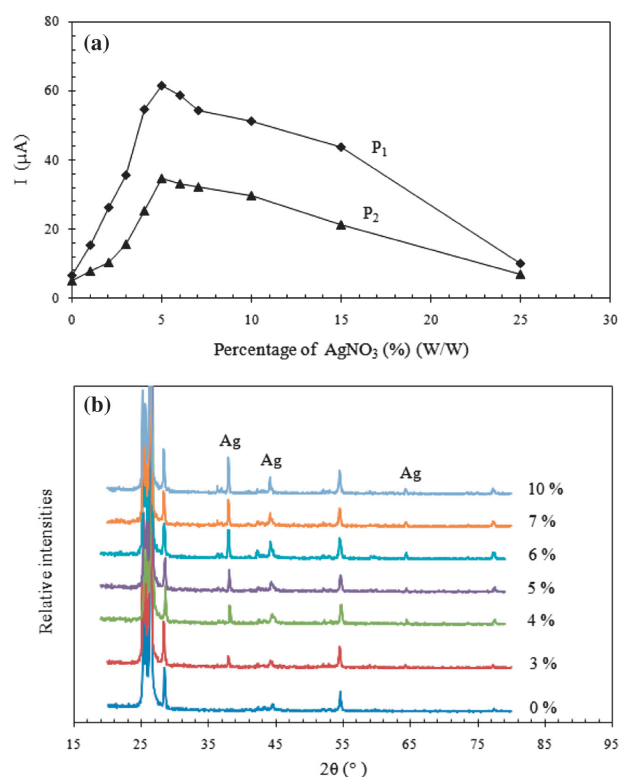
Figure 6 (a) Effect of (AgNO$_3$)/CP ratio on DP of 1.0×10^{-4} - mol L^{-1} paraquat, pH 7.8, tp = 8 min at Ag-CPE. (b) The XRD patterns of the AgNO$_3$/CP heated at 200 °C at different percentages of AgNO$_3$.

voltammetry response, the XRD analysis was investigated. As can be seen, the intensity of formed silver metallic increased with increasing AgNO$_3$ percentage in the carbon paste (Fig. 6b). It can be observed that the particle size of silver in carbon paste increased with the increase in the concentration of silver nitrates initially used. According to previous work, the data obtained shows that synthesis of Ag proceeds via a nucleation and growth type mechanism (Andrew et al., 2011; Golas and Osteryoung, 1987). Higher concentrations of silver
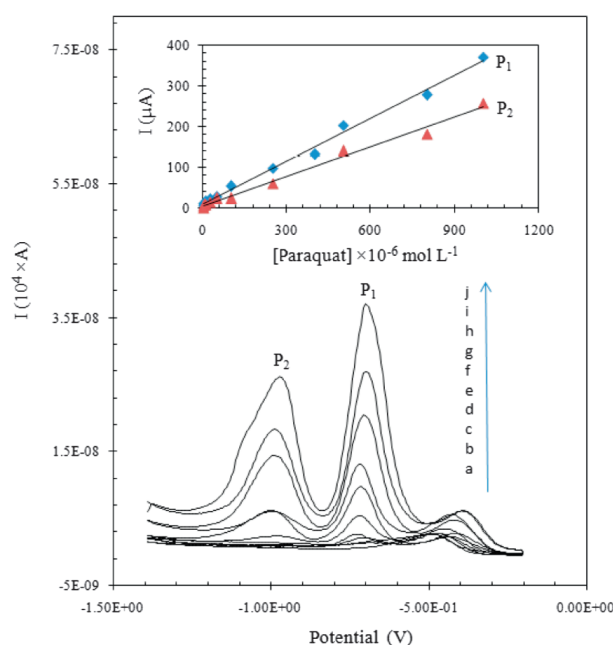

Figure 7 Differential pulse voltammograms in 0.1 mol L^{-1} Na$_2$SO$_4$, pH 7.8, tp = 8 min, at Ag-CPE (5% AgNO$_3$) of different concentrations of paraquat; (a) 1.0×10^{-7}, (b) 1.0×10^{-6}, (c) 1.0×10^{-5}, (d) 2.5×10^{-5}, (e) 5.0×10^{-5}, (f) 1×10^{-4}, (g) 2.5×10^{-4}, (h) 5.0×10^{-4}, (i) 8.0×10^{-4} and (j)1.0×10^{-3} mol L^{-1}.

decreased the peak current significantly, related by the formation of a partial silver film on the CPE electrode (Encarnación et al., 2007). These explain that silver particles, dispersed onto carbon paste, play a role of detector and accumulator for the determination of paraquat. The surface area of AgNO$_3$/CP and CP powders heated at 200 °C was determined by the BET method, and was found to be respectively 16 and 10 m^2 g^{-1}. The small difference between BET values obtained for the carbon and carbon doped with silver, shows that paraquat is highly detected because of the dispersion of silver on the carbon surface. Carbon differs from metals in both its electronic properties and its surface chemistry (McCreery, 1991). Silver can form oxides and hydroxides in aqueous solution resulting in a background current in differential pulse voltammetry (Fig. 1). The presence of oxide raises the possibility of chemical interactions between the surface of silver impregnated carbon paste electrode and paraquat in aqueous solution. These interactions catalyze redox reactions of paraquat and promote adsorption and affect background of differential pulse voltammetry.

3.3. Calibration graph

Under the optimized conditions, the differential pulse as a function of the paraquat concentration was linear between and 1.0×10^{-3} mol L^{-1} (Fig. 7). The regression equation of the linear plot for peaks P$_1$ and P$_2$ were I(P$_1$) = 0.350[PQ] + 7.415 (r^2 = 0.9932) and I(P$_2$) = 0.242 [PQ] + 6.064 (r^2 = 0.9901). The detection limit (DL) and quantification limit (QL) were 3.3×10^{-9} and 10.7×10^{-9} mol L^{-1} for P$_1$ and 6.4×10^{-9} and 21.1×10^{-9} mol L^{-1} for P$_2$. The precision of this methodology
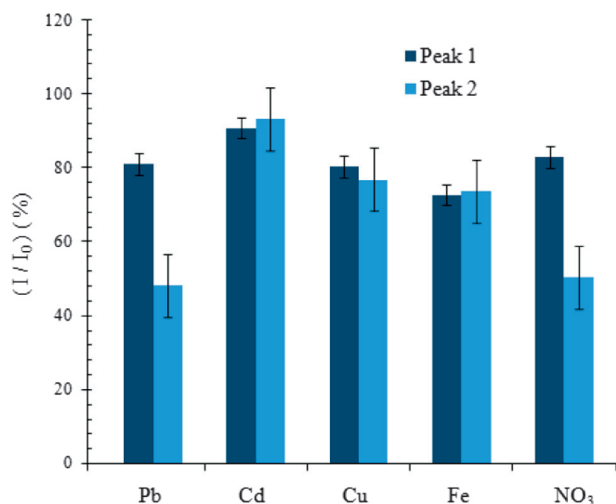
Figure 8 Difference in signal change of 5.0×10^{-5} mol L^{-1} paraquat in the presence of various ions (all at 5.0×10^{-5} mol L^{-1}) under the optimized conditions. The illustrated error bars represent the standard deviations of measurements taken from three independent experiments.

for the determination of paraquat was evaluated for eight successive measurements of the same samples containing 1.0×10^{-4} mol L^{-1} of paraquat. The deviation coefficients were 1.9% and 2.4% for the peaks 1 and 2 respectively. The sensitivity is obviously higher than that of other methods such as spectrophotometry (8.56×10^{-8} mol L^{-1}) (Infante et al., 2008), GC–MS (1.94×10^{-7} mol L^{-1}) (Almeida and Yonamine, 2007) and HPLC (1.94×10^{-8} mol L^{-1}) (Brunetto et al., 2003).

3.4. Interferences studies

The selectivity of the modified electrode for the determination of paraquat(II) was investigated by testing some competing ions, such as Pb^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, and NO_3^- at concentration of 5.0×10^{-5} mol L^{-1} under the same conditions (Fig. 8). The presence of other ions such as Cd^{2+}, Pb^{2+}, Cu^{2+} and Fe^{2+} interferes with the determination of paraquat because of their precipitation with the SO_4^{2-}. The KCN should be added in electrolytic solution to inhibit these interference effects. The
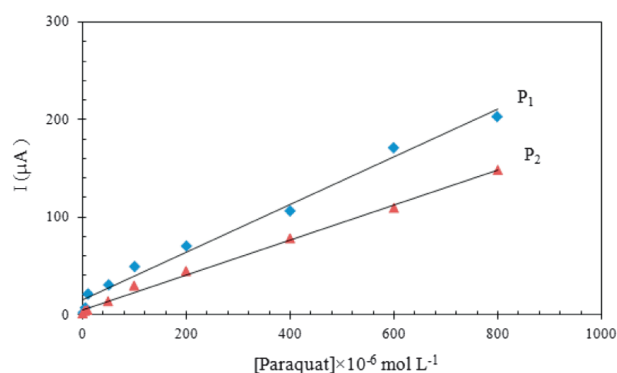
Figure 9 Calibration curves of paraquat in underground water spiked with paraquat in the range from 1.0×10^{-6} to 8.0×10^{-4} mol L^{-1}.

Table 1 Results obtained from the linear regression curves for the determination of PQ(II) at Ag-CPE in underground water.

	Peak 1	Peak 2
r^2	0.985	0.995
Slope A (mol^{-1} L)	0.244	0.179
Detection limit (mol L^{-1}) ($\times 10^{-8}$)	7.2	8.8
Quantification limit (mol L^{-1}) ($\times 10^{-8}$)	23.1	29.4
Relative standard deviation (RSD) (%)	2.5	2.7

NO_3^- ions present a competition with paraquat to interact with silver modified carbon paste electrode and decrease peak currents of paraquat.

3.5. Analytical applications

The proposed method was applied to determine paraquat in underground water. The underground water samples were obtained from a well in the agricultural area in the south of El Jadida (Oualidia, Morocco). The support electrolytes were prepared by addition of 0.1 mol L^{-1} of Na_2SO_4 to fresh underground water. The later sample was analyzed by differential pulse voltammetry and Ag-CPE and there was no paraquat found. To assess the proposed method, some synthetic water samples were prepared by adding appropriate amounts of standard paraquat solution to the underground water. The electroanalytical curves were in the range from 1.0×10^{-6} to 8.0×10^{-4} mol L^{-1} of paraquat. Fig. 9 shows a linear increase in current peak current versus paraquat added into underground sample solution. This behavior indicates that the proposed methodology is suitable for the determination of paraquat in the underground water. The statistical calculations for the assay results showed suitable precision of the proposed method (Table 1). Results obtained for RSD and percentage recovery were, respectively 2.46% and 90.25% obtained for six repetitions in 1.0×10^{-5} mol L^{-1} of paraquat. The proposed method is therefore proven to be suitable for application to complex samples with good repeatability. According to EPA (the US Environmental Protection Agency), (http://www.epa.gov/pesticides/ accessed in October, 2004) the permitted level amount of paraquat in soil and water is 0.1 mg L^{-1}. This shows that the Ag-CPE proved effective for the measurement of the paraquat; the detection limit being below the concentrations permitted by the EPA.

4. Conclusion

The electrochemical behavior of paraquat was evaluated using the voltammetric measurements. The DPV response showed two reduction peaks associated with the partial reduction of paraquat molecule. The influence of the experimental variables involved in the DPV determination of paraquat was investigated. The primary goal, on using Ag–CPE, was to verify the possibility of obtaining responses of paraquat on differential pulse voltammetry. Analytical results show that the proposed modified electrode was able to detect 3.23×10^{-9} mol L^{-1} of paraquat with good sensitivity and repeatability. Additionally, the proposed methodology was successfully applied in determining paraquat in underground water.

Acknowledgement

References

Alden, J.A., Cooper, J.A., Hutchinson, F., Prieto, F., Compton, R.G., 1997. Channel electrode voltammetry and reversible electro-dimerisation processes. The reduction of the methyl viologen di-cation in aqueous solution. J. Electroanal. Chem. 432, 63–70.

Almeida, R.M.D., Yonamine, M., 2007. Gas chromatographic–mass spectrometric method for the determination of the herbicides paraquat and diquat in plasma and urine samples. J. Chromatogr. A 853, 260–264.

Andrew, B., Anand, I.B., Anthony, P.O., Bhargava, Suresh K., 2011. An investigation of silver electrodeposition from ionic liquids: Influence of atmospheric water uptake on the silver electrodeposition mechanism and film morphology. Electrochim. Acta 56, 2895–2905.

Bogusaw, B., Magorzata, J., 2008. The renovated silver ring electrode in determination of lead traces by differential pulse anodic stripping voltammetry. Anal. Chim. Acta 615, 39–46.

Brunetto, M.R., Morales, A.R., Gallignani, M., Burguera, J.L., Burguera, M., 2003. Determination of paraquat in human blood plasma using reversed-phase ion-pair high performance liquid chromatography with direct sample injection. Talanta 59, 913–921.

Bus, J.S., Gibson, J.E., 1984. Paraquat: model for oxidant-initiated toxicity. Environ. Health Perspect. 55, 37–46.

Coasts, G.E., Coasts, G.E., FunderburkJr, H.H., Lawrence, J.M., Davis, D.E., 2006. Factors affecting persistence and inactivation of diquat and paraquat. Weed Res. 6, 58–66.

Dinis-Oliveira, R.J., Remião, F., Carmo, H., Duarte, J.A., Navarro, A.S., Bastos, M.L., Carvalho, F., 2006. Paraquat exposure as an etiological factor of Parkinson's disease. Neurotoxicology 27, 1110–1122.

El Harmoudi, H., Achak, M., Farahi, A., Lahrich, S., El Gaini, L., Abdennouri, M., Bouzidi, A., Bakasse, M., El Mhammedi, M.A., 2013. Sensitive determination of paraquat by square wave anodic stripping voltammetry with chitin modified carbon paste electrode. Talanta 115, 172–177.

Encarnación, B.C.M., Olga, D.R., Julia, A.M.M., 2007. Determination of lamotrigine by adsorptive stripping voltammetry using silver nanoparticle-modified carbon screen-printed electrodes. Talanta 74, 59–64.

Garcia-Febrero, R., -Pablo Salvador, J., Sanchez-Baeza, F., Marco, M.-P., 2014. Rapid method based on immunoassay for determination of paraquat residues in wheat, barley and potato. Food Control 4, 193–201.

Golas, J., Osteryoung, J., 1987. Electrodeposition and anodic stripping of silver on single carbon fibres. Anal. Chim. Acta 192, 225–236.

Gustave, K.D., Charles, P.N., Emmanuel, N., 2012. Amperometric sensors based on sawdust film modified electrodes Application to the electroanalysis of paraquat. Talanta 99, 478–486.

Halfon, E., Galassi, S., Bruggemann, R., Provini, A., 1996. Selection of priority properties to assess environmental hazard of pesticides. Chemosphere 33, 1543–1562.

Hausburg, M.A., DeKrey, G.K., Salmen, J.J., Palic, M.R., Gardiner, C.S., 2005. Effects of paraquat on development of preimplantation embryos in vivo and in vitro. Reprod. Toxicol. 20, 239–246.

Hepel, M., Osteryoung, R.A., 1983. Cathodic stripping analysis complicated by adsorption processes: determination of 2-thiouracil at rotating silver electrode. J. Electroanal. Chem. Interfacial Electrochem. 149, 193–211.

Huggins, D.R., Reganold, J.P., 2008. No-till: the quiet revolution. Sci. Am., 70–77.

Hughes, J.T., 1988. Brain damage due to paraquat poisoning: a fatal case with neuropathological examination of the brain. Neurotoxicology 9, 243–248.

Infante, C.M.C., Morales-Rubio, A., Guardia, M.D.I., Rocha, F.R.P., 2008. A multicommuted flow system with solenoid micro-pumps for paraquat determination in natural waters. Talanta 75, 1376–1381.

Kim, Y.-J., Hong, Y.-C., Lee, K.-H., Park, H., Park, E.A., Moon, H.-S., Ha, E.-H., 2005. Oxidative stress in pregnant women and birth weight reduction. Reprod. Toxicol. 19, 487–492.

Kreisig, S., Tarazona, A., Koglin, E., 1997. The adsorption of paraquat on silver electrode surfaces: a SiZRS microprobe study. Electrochim. Acta 42, 3335–3344.

Lovric, M., Komorsky-Lovric, S., 1988. Square-wave voltammetry of an adsorbed reactant. J. Electroanal. Chem. 248, 239–253.

Madeley, J., 2002. Paraquat-Syngenta's controversial herbicide, A written report for Berne Declaration, Swedish Society for Nature conservation, Pesticide Action Network UK, Pesticide Action Network Asia Pacific, and Foro Emaús, pp. 1–28.

McCreery, R.L., 1991. Carbon electrodes: structural effects on electron transfer kinetics. Electroanal. Chem. 17, 221–373.

Norberto, C.P., Enrique, M.O., Dawn, M.B., 2008. Quantitative determination of paraquat in meconium by sodium borohydride-nickel chloride chemical reduction and gas chromatography/mass spectrometry (GC/MS). J. Chromatogr. B 862, 93–99.

Rameshbabu, N., Sampath Kumar, T.S., Prabhakar, T.G., Sastry, V.S., Murty, K.V.G.K., Prasad Rao1, K., 2007. Antibacterial nanosized silver substituted hydroxyapatite: Synthesis and characterization. J. Biomed. Mater. Res., Part A 80, 581–591.

Souza, D.D., Machado, S.A.S., Pires, R.C., 2006. Multiple square wave voltammetry for analytical determination of paraquat in natural water, food, and beverages using microelectrodes. Talanta 69, 1200–1207.

Suntres, Z.E., 2002. Role of antioxidants in paraquat toxicity. Toxicology 180, 65–77.

Walcarius, A., Lambers, L., 1996. Square wave voltammetric determination of paraquat and diquat in aqueous solution. J. Electroanal. Chem. 406, 59–68.

Zou, Y., Shi, Y., Bai, Y., Tang, J., Chen, Y., Wang, L., 2011. An improved approach for extraction and high-performance liquid chromatography analysis of paraquat in human plasma. J. Chromatogr. B 879, 1809–1812.

http://www.epa.gov/pesticides/ accessed in October 2004.