



Original scientific paper

Electrochemical behaviour and voltammetric determination of p-phenylenediamine at carbon paste electrode

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Received: April 18, 2017; Revised: June 26, 2017; Accepted: July 26, 2017

Abstract

An electrochemical method was developed for voltammetric determination of p-phenylenediamine using a carbon paste electrode (CPE). The electrode exhibited the highest electrocatalytic activity toward oxidation and reduction of p-phenylenediamine in the phosphate buffer, pH 7. After optimizing the experimental conditions and square wave voltammetry parameters, a linear current response toward concentration of p-phenylenediamine was obtained in the range of 0.12–3.00 μM with detection limit of 0.071 μM . The proposed procedure was successfully applied for determination of the total p-phenylenediamine content in the takeout extract sample.

Keywords

p-phenylenediamine; electroanalysis; voltammetry

Introduction

p-phenylenediamine (p-PD) is an aromatic diamine and derivative of the aniline with the chemical structure presented in Figure 1. It is commonly used in the manufacture of dyestuffs, as hair dye and as adjuvant of henna [1,2], in several industries, dyeing furs, photochemical processes, cosmetic and fabrication of household goods [3,4]. Toxic effects of p-PD, however, have also been reported by several authors [5-8].

Many analytical methods, including gas chromatography coupled mass spectrometry (GC-MS) [9,10], gas chromatography (GC) [11], and high-performance liquid chromatography (HPLC) [2] have already been reported for the determination of p-PD. Although chromatographic methods are sensitive and reliable, they have some disadvantages such as being time and labour consuming, expensive and demanding for sample pre-treatments and qualified personnel. Promising alternatives in this regard have been found in the electroanalytical methods which can offer high sensitivity, rapid response, easy operation and low cost [12].

Though the electrochemical properties of p-PD have been investigated at glassy carbon [13,14] and carbon paste electrodes [15-18], most of these studies were mainly concerned on the mechanism of p-PD polymerization. Although several studies on the detection of some similar compounds in medical plants [19,20] and drugs [21,22] were already published, the direct electroanalytical determination of p-PD on carbon paste electrode has not been reported previously.

In this paper, we report on the electrochemical properties of p-PD on the surface of carbon paste electrode and this electrode will also be applied for the determination of p-PD content in the plant of takeout.

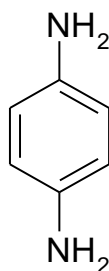


Figure 1. Chemical structure of p-phenylenediamine

Experimental

Apparatus

Electrochemical experiments were carried out with an Autolab (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N potentiostat/galvanostat controlled by GPES 4.9 software. A three-electrode electrochemical cell was employed for all electrochemical measurements. Carbon paste electrode (4 mm diameter) served as the working electrode, a platinum plate as the counter electrode, and Ag/AgCl (3 mol/L KCl) as the reference electrode, respectively. The pH of the buffer solutions was measured using a Fisher Scientific Accumet AB15 BASIC pH-meter.

Reagents

All chemicals used were of analytical grade. P p-PD and graphite were purchased from Sigma and Fluka, respectively. Sodium hydroxide, NaOH, $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \times 2\text{H}_2\text{O}$ powders were purchased from Riedel-de Haën. All aqueous solutions were prepared in distilled water. The pH was adjusted with NaOH. A p-PD stock solution of 1 mM was prepared by dissolving p-PD in the phosphate buffer solution (PBS) before use in measurements.

Preparation of the carbon paste electrode

The carbon paste electrode (CPE) was prepared by mixing 1 g of graphite powder and 0.3 mL of paraffin oil using a mortar and pestle until a homogenous paste was obtained. The paste was then incorporated into the electrode cavity (4 mm diameter) and polished by a smooth paper. Prior each measurement, the electrode surface was renewed.

Sample preparation

Takeout plant (*Tamarix aphylla*) samples were obtained from Zagora region, Morocco. The samples were firstly grounded by a crusher, then 1 g of the powder was weighed, dissolved in 50 mL of ethanol, and placed in a mounting reflux for 2 h. After filtration, the solvent was evaporated by a rotavapor and an amount of the filtrate (108 mg) was dissolved directly in 100 mL of 0.1 M phosphate buffer solution (PBS), pH 7.0 for the final determination of the p-PD content.

Analytical procedure

The electrochemical cell containing 1 mM of p-PD dissolved in 0.1 M PBS, pH 7.0 was prepared. After that, the CPE electrode was placed in the test solution and the cyclic voltammetry was applied between -0.2 and 0.8 V at a scan rate of 50 mV s^{-1} . The parameters of SWV of all measurements were, step potential 5 mV, amplitude 50 mV and frequency 50 Hz. The calibration curve of p-PD concentrations was illustrated by SWV in the range of $0.12\text{--}3.0 \text{ }\mu\text{M}$ under the optimized conditions, and then used for directly determination to the amount of p-PD in the sample of takeout extracts.

Results and discussion

Electrochemical behaviour of *p*-phenylenediamine

The electrochemical behaviour of 1 mM p-PD on a CPE in the 0.1 M, pH 7.0 PBS was investigated using cyclic voltammetry at a scan rate of 50 mV s^{-1} . Whilst not any response is observed for the CPE in the blank solution (Fig. 2a), a pair of well-defined redox waves are observed in presence of 1 mM p-PD in 0.1 M, pH 7 PBS (Fig. 2b). The anodic, E_{pa} , and cathodic, E_{pc} , potentials are situated at $E_{pa} = 0.10 \text{ V}$ and $E_{pc} = 0.03 \text{ V}$, respectively. In general, presence of a peak in the reverse potential scan indicates reversibility of the oxidation process on the surface of the electrode.

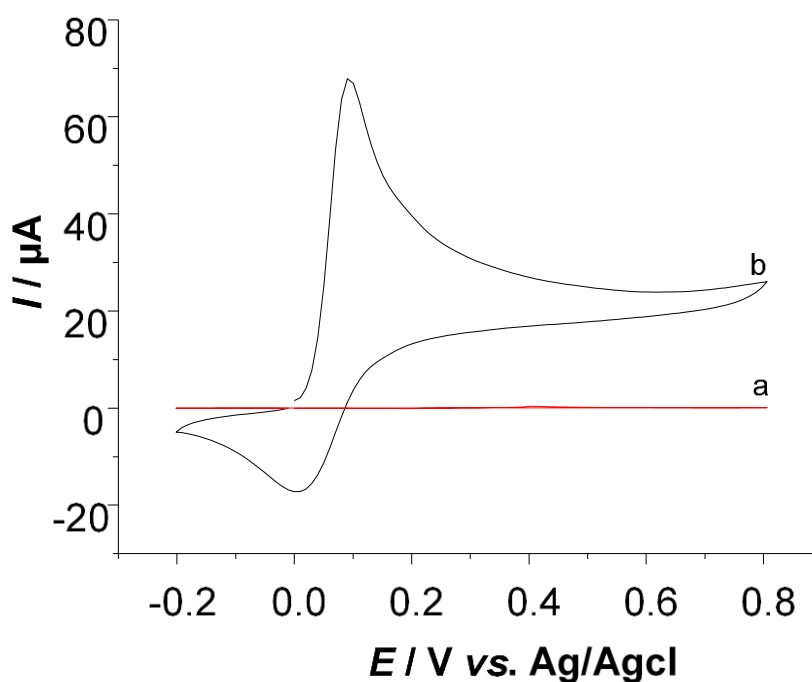
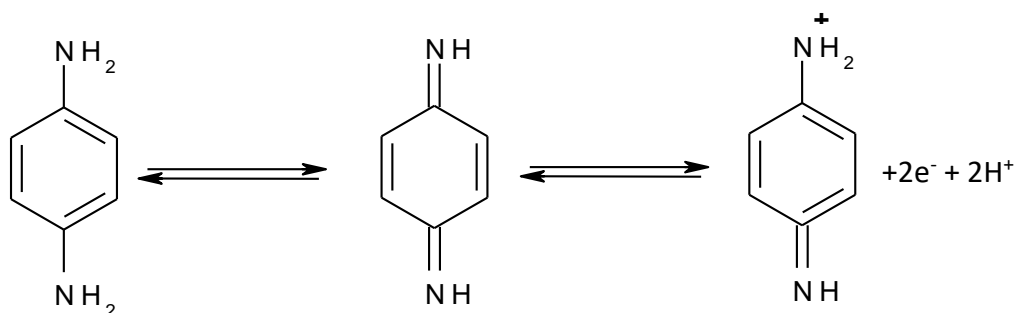


Figure 2. Cyclic voltammograms of CPE recorded at 50 mV s^{-1} in blank (a) and for 1 mM p-PD in 0.1 M, pH 7.0 PBS (b).

The oxidation mechanism of *p*-phenylenediamine on the electrode surface

The redox reaction of p-PD belongs to a class of two-electron and two-proton processes [23]. Possible oxidation mechanism of p-PD is shown in the Scheme 1. After formation of radical cation from the amino group, electrons are delocalized over the cycle forming another cation from the second amino group, while by elimination of two protons, the oxidized p-PD is formed. The mesomeric effect of nitrogen atom plays an important role, and electron density increases at π -bond and hence oxidation becomes easy.



Scheme 1. The oxidation mechanism of *p*-phenylenediamine

Effect of buffer pH

The effect of pH of the PBS on the electrochemical behaviour of *p*-PD was studied in the pH range of 3.0–10.0. Fig. 3 shows that as pH value of the solution was increased, the redox peak is shifted negatively what indicates involvement of protons in the redox reaction [24]. Depending on a pH ranging from 3 to 7, the formal potential (E^0) for the anodic and cathodic peaks changed linearly. The redox current values increased from pH 3.0 and reached a maximum at pH 7.0 (curve e in Fig. 3). Therefore, the PBS, pH 7.0 was selected as the optimum working solution which will offer a higher peak resolution of *p*-PD and relatively higher current response.

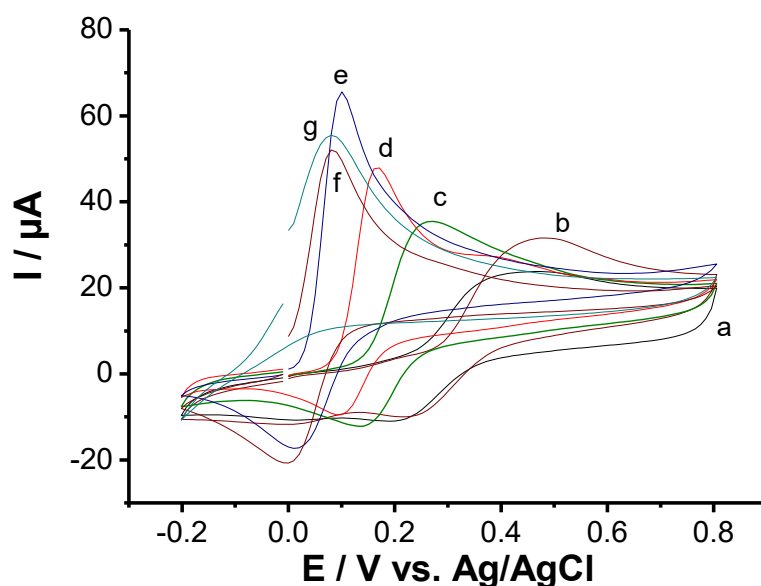


Figure 3. Cyclic voltammograms of CPE recorded at 50 mV s^{-1} for 1 mM *p*-PD in PBS having pH 3–10: a - 3, b - 4, c - 5, d - 6, e - 7, f - 8, g - 10.

Effect of potential scan rate

Fig. 4 shows the cyclic voltammograms of *p*-PD at CPE in the PBS, pH 7.0, recorded at the scan rates varied from 20 to 400 mV s^{-1} . As is seen in the inset of Fig. 4, the redox peak currents at the CPE in the solution containing *p*-PD increased linearly with the scan rate in the range from 50 to 250 mV s^{-1} , what indicates the adsorption-controlled redox process. The linear regression equations can be defined as:

$$I_{pa} / \mu\text{A} = 71.76 + 0.36 \nu (\text{mV s}^{-1}) \quad (R^2 = 0.995)$$

$$I_{pc} / \mu\text{A} = 18.30 - 0.37 \nu (\text{mV s}^{-1}) \quad (R^2 = 0.996)$$

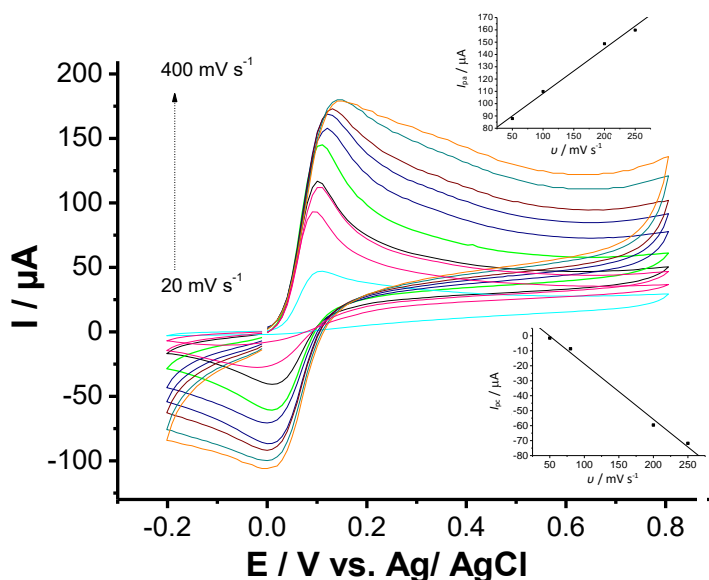


Figure 4. Cyclic Voltammograms of CPE for 1 mM p-PD in PBS, pH 7.0, recorded at scan rates (ν) of 20, 50, 80, 100, 150, 200, 250, 300, 350 and 400 mV s^{-1} . Inset: plots of peak currents (I_{pa} and I_{pc}) vs. scan rate (ν) in the range from 50 to 250 mV s^{-1} .

Effect of the square wave voltammetry (SWV) parameters and accumulation conditions

The effect of the accumulation potential in SWV measurements was investigated between -0.2 V and 0.1 V at the accumulation time of 30 s. As shown in Fig. 5A, the peak current values decreased significantly when the accumulation potential was shifted to potentials more positive than -0.1 V, because the p-PD adsorbed on the electrode becomes oxidized. Therefore, -0.1 V was used as the accumulation potential. Similarly, the effect of accumulation time was studied in the 30–240 s range at the accumulation potential of -0.1 V. Fig. 5B shows firstly a rapid increase in peak current values with increase of the accumulation time, then a maximum is reached at 120 s and after that, the constant values obtained indicate the saturation of the electrode surface by adsorbed layer. Therefore, 120 s was used as the proper accumulation time.

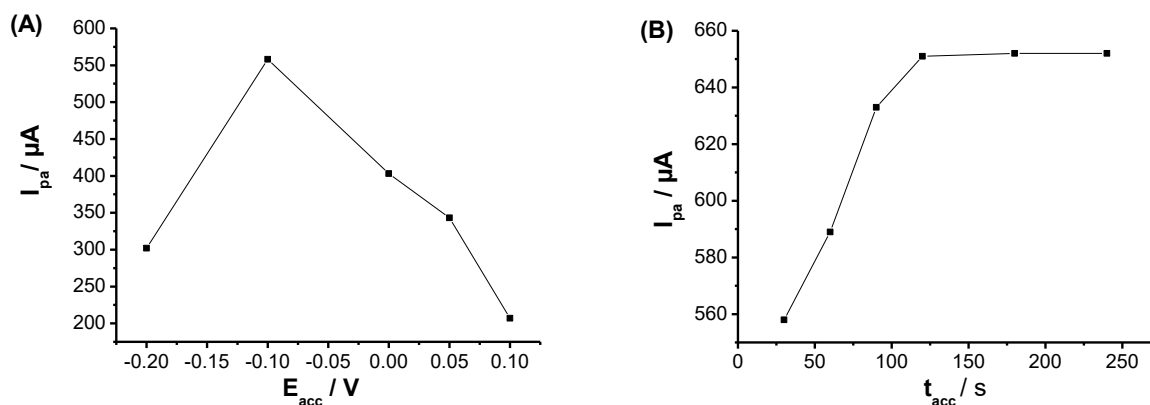


Figure 5. A - Effect of accumulation potential (-0.2 V to 0.1 V) to I_{pa} values of SWV responses measured for the accumulation time of 30 s; **B** - Effect of accumulation time (30 s to 240 s) to I_{pa} values of SWV responses measured at the accumulation potential of -0.1 V.

Calibration curve

The relationship between the peak current and concentration of p-PD was studied at the CPE by using SWV under the optimized conditions. Fig. 6 shows that the peak current values were linearly

related to the concentration of p-PD in the range of 0.12–3.0 μM . The linear regression equation was defined as: $I_{pa} / \mu\text{A} = 0.181 + 0.241 C / \mu\text{M}$, with the correlation coefficient of 0.999.

The detection limit calculated as $(3\sigma/p)$ was 0.071 μM , where σ and p are the standard deviation of the blank and the slope of the calibration graph, respectively. The relative standard deviation (RSD) for repetitive measurements of 1.5 μM p-PD was found to be 3.49 % (five replicates), suggesting that the electrode demonstrated excellent repeatability.

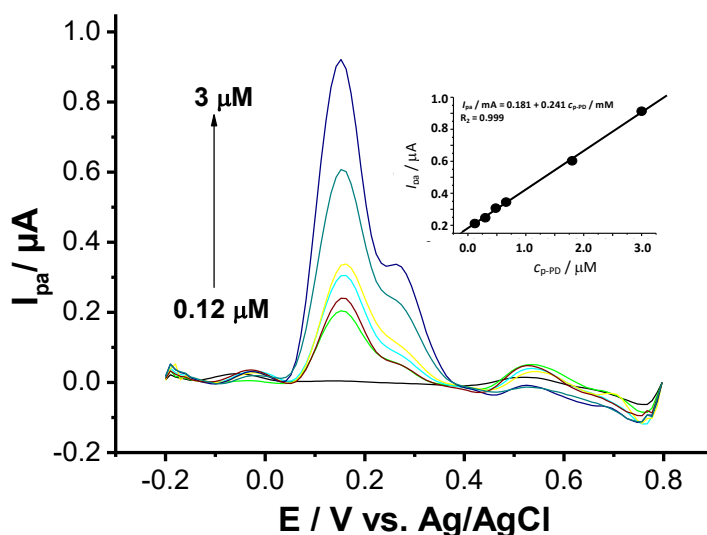


Figure 6. SWV responses of CPE in 0.1 M PBS, pH 7.0 and various concentrations of p-PD in the range 0.12–3.0 μM . Inset: linear calibration curve of peak current (I_{pa}) versus p-PD concentration

Interference study

To evaluate possible interference of some foreign species on the determination of p-PD, a systematic study was carried out. Data listed in Table 1 show the p-PD peak current ratios in the presence and absence of respective interferents. It seems that presence of 1.5 μM Mg^{2+} , K^+ , Na^+ and Zn^{2+} did not affect the determination of p-PD. On the other hand, presence of 1.5 μM Cu^{2+} showed a slight interference. In general, despite the high redox potential used for p-PD detection, the interference study showed promising results for its selective determination.

Table 1. Effect of some foreign species on the peak current response of 0.3 μM p-PD in PBS, pH 7 at a fivefold concentration of interferent cations.

Interfering compound	Peak current ratio
Mg^{2+}	1.013
Zn^{2+}	0.760
K^+	1.050
Na^+	1.050
Cu^{2+}	1.330

Analytical application

The CPE was used to determine the amount of p-PD in the takeout extracts. The results are shown in Table 2. Recovery measurements were made by adding known amounts of the standard p-PD solution to the previously analyzed samples. The recovery for determination of p-PD was 110 %. The recovery indicated that the accuracy of the proposed method is acceptable.

Following the sample preparation, measurements were performed similarly to those of standard p-PD solutions. The total p-PD contents were determined by using the former calibration curve equation. The total measured p-PD content of the takeout sample (w/w) was determined as 1 %.

Table 2. Determination of p-PD in plant takeout extract sample.

Sample	Detected	Amount of p-DP, μM			Recovery, %
		Added	Expected	Found	
Takaout extract	0.54	1.5	2.04	2.25	110

Conclusions

In this paper, a simple, rapid, and sensitive determination of p-phenylenediamine in the phosphate buffer solution, pH 7.0 using the carbon paste electrode was proposed. A pair of well-defined redox peaks was obtained at the electrode. Under optimized conditions, the electrode showed excellent performance in terms of detection limit, linearity range, selectivity, repeatability, and recovery values. The proposed method was successfully applied for the determination of the total content of p-phenylenediamine in the plant of takeout sample.

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