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Voltammetric determination of carbidopa and folic acid using a modified carbon nanotubes paste electrode

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Abstract: A novel electrochemical sensor for the selective and sensitive detection of carbidopa in the presence of a large excess of folic acid at physiological pH was developed by the bulk modification of a carbon paste electrode (CPE) with carbon nanotubes (CNTs) and vinylferrocene. Large peak separation, good sensitivity and stability allow this modified electrode to be used for the analysis of carbidopa individually and simultaneously along with folic acid. Applying square wave voltammetry (SWV), a linear dynamic range of 1.0×10^{-6}–7.0×10^{-4} M with a detection limit of 2.0×10^{-7} M was obtained for carbidopa. Finally, the proposed method was applied to the determination of carbidopa and folic acid in a urine sample.

Keywords: carbidopa; folic acid; carbon nanotubes; modified electrodes.

INTRODUCTION

Carbon nanotubes (CNTs) have received enormous attention in the last years due to their unique structural, mechanical, geometric and chemical properties.[1] Their closed topology and tubular structure have made them very attractive materials.[2,3] CNTs have demonstrated themselves to be extremely useful for the development of new electrode materials. Their electrocatalytic properties have been widely demonstrated in connection with several compounds of clinical, biological and environmental interest.[4–17]

In addition, the application of chemically modified electrodes (CMEs) in electroanalysis offers several advantages. They can lower the overpotential, increase the reaction rate and sensitivity and improve selectivity.[18–27]

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Carbidopa (lodosyn) is a drug used in the treatment of Parkinson's disease by inhibiting the peripheral metabolism of levodopa.[28] A combination of carbidopa/levodopa carries the brand names sinemet, parcopa and atamet; while stalevo is a combination with entacapone, which enhances the bioavailability of carbidopa and levodopa. Therefore, determination of this drug is very important in biological sample such as urine. Different techniques have been employed for the determination of carbidopa, including spectrophotometry, capillary zone electrophoresis, high performance liquid chromatography (HPLC) and liquid chromatography (LC). Long analysis times, the use of organic solvents and high costs are some of the drawbacks associated with these techniques. Voltammetry is considered as an important electrochemical technique utilized in electroanalytical chemistry because it provides low cost, sensitivity, precision, accuracy, simplicity and rapidity.[29–35]

Folic acid, often regarded as a part of the vitamin B complex, possesses considerable biological importance for human health, especially during periods of rapid cell division and growth.[36] A deficiency of general folic acid may cause serious illness, notably for women planning pregnancy, which can result in malformations of the spine, skull, and brain.[37] Therefore, the determination of folic acid has drawn significant attention, and a reliable and sensitive detection method is widely anticipated. At present, some techniques, such as spectrophotometry, fluorometry, HPLC, and flow injection chemiluminescence have been used to detect folic acid.[38] However, these techniques are complex, time-consuming, and require expensive instruments. Electrochemical methods have also been used and have attracted enormous interest due to their advantages of simplicity, rapid response, excellent reproducibility, good stability, low cost, low detection limit, *etc*.[39–42]

In the present study, a new electrode composed of a carbon nanotube paste electrode (CNPE) modified with vinylferrocene (VFCNPE) was prepared and its performance for the electrocatalytic determination of carbidopa in aqueous solutions investigated. The analytical performance of the modified electrode for quantification of carbidopa in the presence of folic acid was also evaluated.

EXPERIMENTAL

Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302 N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three-electrode cell was used at 25±1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the VFCNPE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 827 pH/ion meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. Carbidopa, folic acid and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder (particle diameter = 0.1 mm) and paraffin oil (DC 350, density = 0.88 g cm^{-3}) as the

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binding agent (both from Merck) were used for preparing the pastes. Multiwalled carbon nanotubes (purity more than 95 %) with o. d. between 10 and 20 nm, i. d. between 5 and 10 nm, and tube length from 0.5 to 200 μm were prepared by Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0. Vinylferrocene (VF) was purchased from Sigma Aldrich.

Preparation of the electrode

The VFCNPEs were prepared by hand mixing 0.01 g of VF with 0.89 g graphite powder and 0.1 g CNTs with a pestle and mortar. Then, *ca*. 0.7 mL of paraffin oil was added to this mixture and mixed for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube (*ca.* 3.4 mm i. d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper.

For comparison, a VF modified CPE electrode (VFCPE) without CNTs, a CNTs paste electrode (CNPE) without VF, and an unmodified CPE in the absence of both VF and CNTs were also prepared in the same way.

RESULTS AND DISCUSSION

Electrochemical properties of VFCNPE

A VFCNPE was constructed and its electrochemical properties were studied in a 0.1 M phosphate buffer solution (PBS, pH 7.0) using cyclic voltammetry (CV). The experimental results showed well defined and reproducible anodic and cathodic peaks related to the vinylferrocene/vinylferricenium ion redox system, with E_{pa}, E_{pc} and $E^{\circ\prime}$ of 0.41, 0.3 and 0.355 V *vs.* Ag/AgCl/KCl (3.0 M), respectively. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 110 mV, was greater than the value of $59/n$ mV expected for a reversible system,[43] suggesting that the redox couple of VF in the VFCNPE had a quasi-reversible behavior in aqueous medium.

Influence of pH

The electrochemical behavior of carbidopa was dependent on the pH value of the aqueous solution, whereas the electrochemical properties of the Fc/Fc^+ redox couple were independent of pH. Therefore, pH optimization of the solution was necessary in order to obtain the electrocatalytic oxidation of carbidopa. Thus the electrochemical behavior of carbidopa was studied in 0.1 M PBS at different pH values ($2.0 < pH < 11.0$) at the surface of VFCNPE by CV. It was found that the electrocatalytic oxidation of carbidopa at the surface of VFCNPE was more favored under neutral conditions than in acidic or basic medium. This appears as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current in the CVs of VFCNPE. Thus, the pH 7.0 was chosen as the optimum pH for electrochemical oxidation of carbidopa at the surface of a VFCNPE.

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In addition, pH optimization of the solution was necessary in order to obtain the best peak resolution for carbidopa and folic acid. Thus, the electrochemical behavior of carbidopa and folic acid was studied in 0.1 M PBS at different pH values (2.0 < pH < 11.0) at the surface of VFCNPE by square wave voltammetry (SWV). It was found that the best condition to separate oxidation peaks of carbidopa and folic acid was pH 7.0. Thus, the pH 7.0 was chosen as the optimum pH for simultaneous determination of carbidopa and folic acid.

Electrocatalytic oxidation of carbidopa at a VFCNPE

The CV responses for the electrochemical oxidation of 0.4 mM carbidopa at an unmodified CPE (curve b), a CNPE (curve d), a VFCPE (curve e) and a VFCNPE (curve f) are depicted in Fig. 1. As can be seen, while the anodic peak potentials for carbidopa oxidation at the CNPE, and unmodified CPE were 700 and 750 mV, respectively, the corresponding potentials at the VFCNPE and VFBCPE were ≈410 mV. These results indicate that the peak potential for carbidopa oxidation at the VFCNPE and VFCPE is shifted by ≈290 and 340 mV toward negative values compared to the peak potentials at the CNPE and unmodified CPE, respectively. However, the VFCNPE showed a much higher anodic peak current for the oxidation of carbidopa compared to the VFCPE, indicating that the combination of CNTs and the mediator (VF) significantly improved the performance of the electrode toward carbidopa oxidation. In fact, VFCNPE in the absence of carbidopa exhibited a well-behaved redox reaction (Fig. 1, curve c) in 0.1 M PBS (pH 7.0). However, there was a drastic increase in the anodic peak current in the presence of 0.4 mM carbidopa (curve f), which could be related to the strong electrocatalytic effect of the VFCNPE towards this compound.[43]

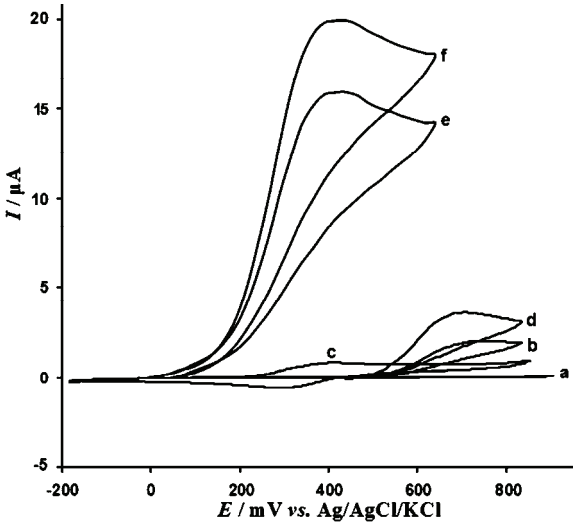

Fig. 1. CVs of: a) unmodified CPE in 0.1 M PBS (pH 7.0), b) unmodified CPE in 0.4 mM carbidopa, c) VFCNPE in 0.1 M PBS, d) CNPE in 0.4 mM carbidopa, e) VFCPE in 0.4 mM carbidopa and f) VFCNPE in 0.4 mM carbidopa. In all cases, the scan rate was 10 mV s^{-1}.

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The effect of scan rate on the electrocatalytic oxidation of carbidopa at the VFCNPE was investigated by CV (Fig. 2). As could be observed in Fig. 2, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming kinetic limitation in the electrochemical reaction. Furthermore, a plot of peak height (I_p) *vs*. the square root of the scan rate ($v^{1/2}$) was found to be linear in the range of 6–16 mV s^{-1}, suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 2A).

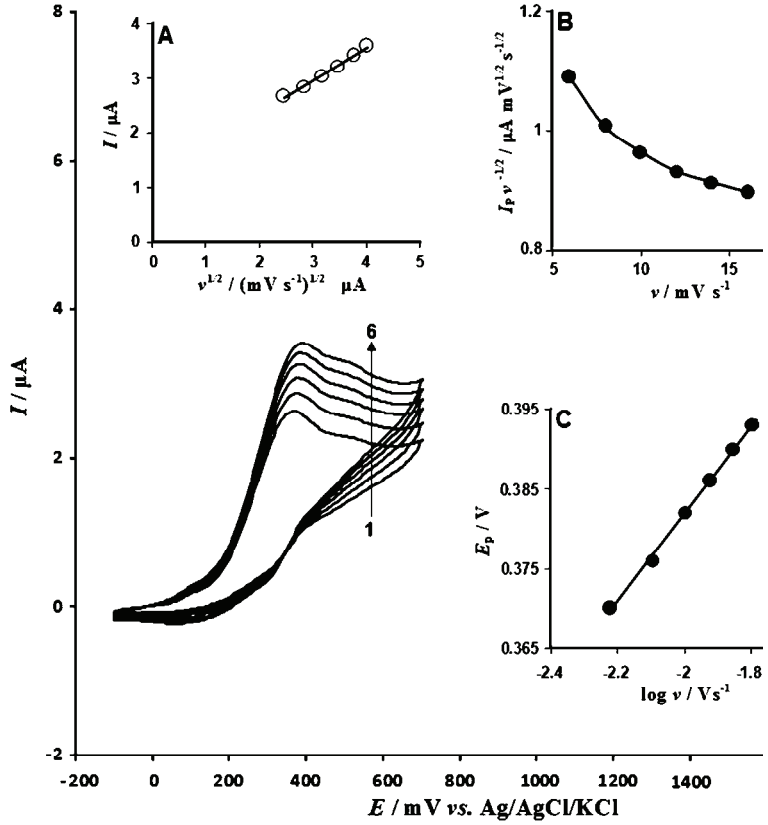

Fig. 2. CVs at the VFCNPE in 0.1 M PBS (pH 7.0) containing 100.0 µM carbidopa at various scan rates; Numbers 1–6 correspond to of 6, 8, 10, 12, 14 and 16 mV s^{-1}, respectively. Insets: variation of: A) anodic peak current *vs*. $v^{1/2}$, B) normalized current ($I_p/v^{1/2}$) *vs*. *v* and C) anodic peak potential *vs*. log *v*.

A plot of the scan rate-normalized current (($I_p/v^{1/2}$)) *vs*. scan rate (Fig. 2B) exhibited the characteristic shape typical of an EC′ process.[43]

The Tafel slope (*b*) could be obtained from the slope of E_p *vs*. log *v* using Eq. (1):[43]

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$$E_p = \frac{b}{2}\log v + \text{constant} \quad (1)$$

The Tafel slope was found to be 0.109 V (Fig. 2C), which indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient (α) of 0.46.

Chronoamperometric measurements

Chronoamperometric measurements of carbidopa at the VFCNPE were performed by setting the working electrode potential at 0.5 V *vs*. Ag/AgCl/KCl (3.0 M) for various concentration of carbidopa in PBS (pH 7.0), Fig. 3. For an electroactive material (carbidopa in this case) with a diffusion coefficient of *D*, the current observed for the electrochemical reaction under mass transport limited conditions is described by the Cottrell equation.[43] Experimental plots of *I vs.* $t^{-1/2}$ were employed, with the best fits for different concentrations of carbidopa (Fig. 3A). The slopes of the resulting straight lines were then plotted *vs*. the carbidopa concentration (Fig. 3B). From the resulting slope and the Cottrell equation, the mean value of the *D* was found to be 1.7×10^{-6} cm^2 s^{-1}.

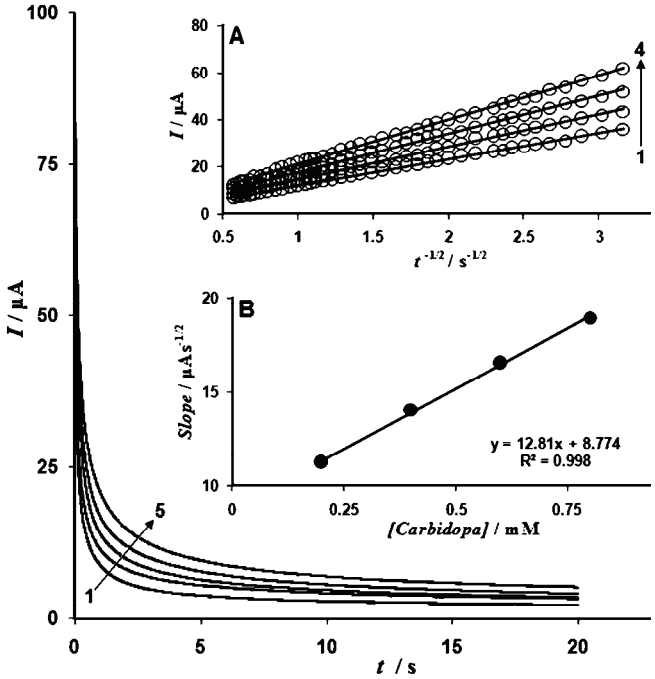

Fig. 3. Chronoamperograms obtained at the VFCNPE in 0.1 M PBS (pH 7.0) for different concentration of carbidopa. The numbers 1–5 correspond to 0.0, 0.2, 0.4, 0.6 and 0.8 mM of carbidopa. Insets: A) plots of *I vs.* $t^{-1/2}$ obtained from the chronoamperograms 2–5 and B) plot of the slope of the straight lines against the carbidopa concentration.

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Calibration plot and limit of detection

The SWV method was used to determine the concentration of carbidopa (Fig. 4; initial potential = 0.05 V, end potential = 0.7 V, step potential = 0.001 V, amplitude = 0.02 V, frequency = 10 Hz). The plot of peak current *vs*. carbidopa concentration consisted of two linear segments with slopes of 0.220 and 0.021 μA μM^{-1} in the concentration ranges of 1.0–10.0 μM and 10.0–700.0 μM, respectively. The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitations.[43] The detection limit (3σ) of carbidopa was found to be 0.2 μM.

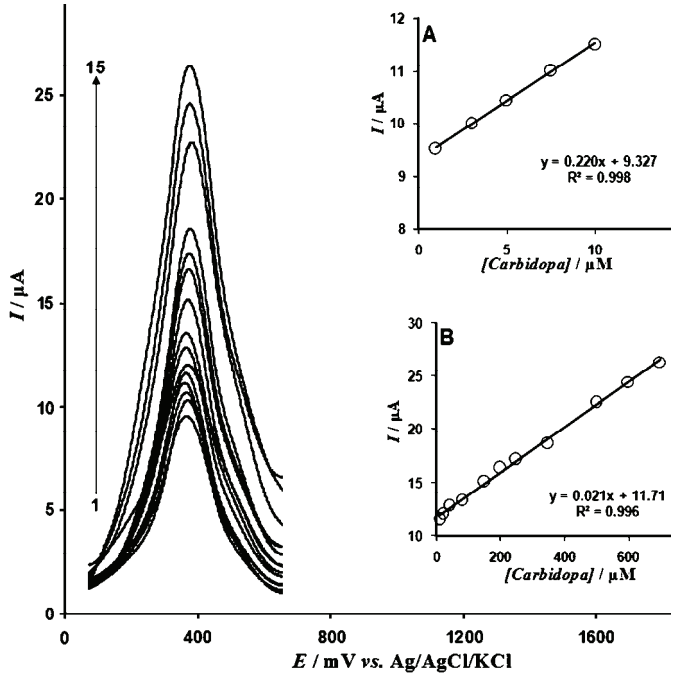

Fig. 4. SWVs of the VFCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of carbidopa. Numbers 1–15 correspond to 1.0, 3.0, 5.0, 7.5, 10.0, 20.0, 40.0, 80.0, 150.0, 200.0, 250.0, 350.0, 500.0, 600.0 and 700.0 μM of carbidopa. Insets: plots of the electrocatalytic peak current as a function of carbidopa concentration in the range of 1.0–10.0 μM (A) and 10.0–700.0 μM (B).

Simultaneous determination of carbidopa and folic acid

One of the main objectives of this study was to detect carbidopa and folic acid simultaneously using the VFCNPE. The determination of carbidopa and folic acid in mixtures was performed at the VFCNPE using SWV. The concentration of folic acid was varied, while keeping the carbidopa concentration constant. The results are shown in Fig. 5 (initial potential = –0.1 V, end potential =

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= 1.1 V, step potential = 0.001 V, amplitude = 0.02 V, frequency = 10 Hz). When the concentration of carbidopa was kept constant at 500.0 μM, the peak current of folic acid was proportional to its concentration from 100.0 μM –1200.0 μM. No changes in the peak current and potential of carbidopa could be observed.

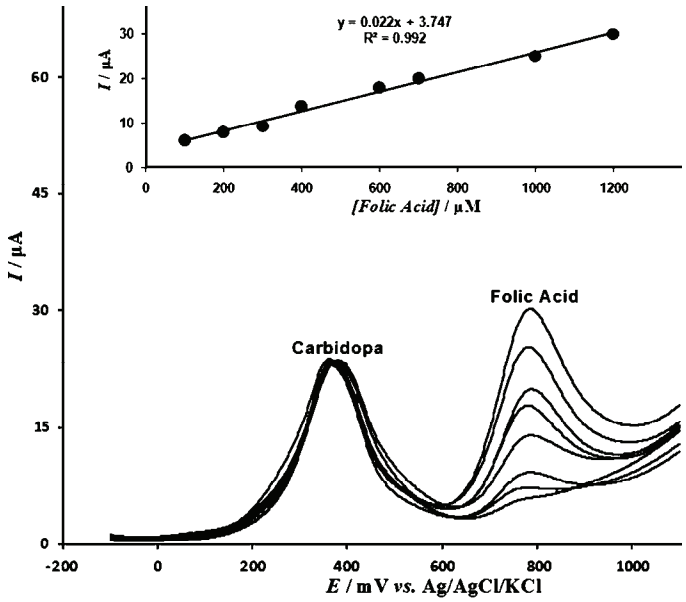

Fig. 5. SWVs at the VFCNPE in 0.1M PBS (pH 7.0) containing 500.0 μM carbidopa and different concentrations of folic acid (from inner to outer): 100.0, 200.0, 300.0, 400.0, 600.0, 700.0, 1000.0 and 1200.0 μM. Inset: plot of the electrocatalytic peak current as a function of folic acid concentration.

Furthermore, experiments were performed in which the concentrations of carbidopa and folic acid were simultaneously changed, and the SWVs recorded (initial potential = 0.02 V, end potential = 0.93 V, step potential = 0.001 V, amplitude = 0.02 V, frequency = 10 Hz). The voltammetric results showed well-defined anodic peaks at potentials of 390 and 780 mV, corresponding to the oxidation of carbidopa and folic acid, respectively, indicating that the simultaneous determination of these compounds at the VFCNPE is feasible, as shown in Fig. 6.

The sensitivity of the modified electrode towards the oxidation of carbidopa was found to be 0.022 μA μM^{-1}. This is equal to the value obtained in the absence of folic acid, indicating that the oxidation processes of these compounds at the VFCNPE are independent and therefore, the simultaneous determination of their mixtures is possible without significant interferences.

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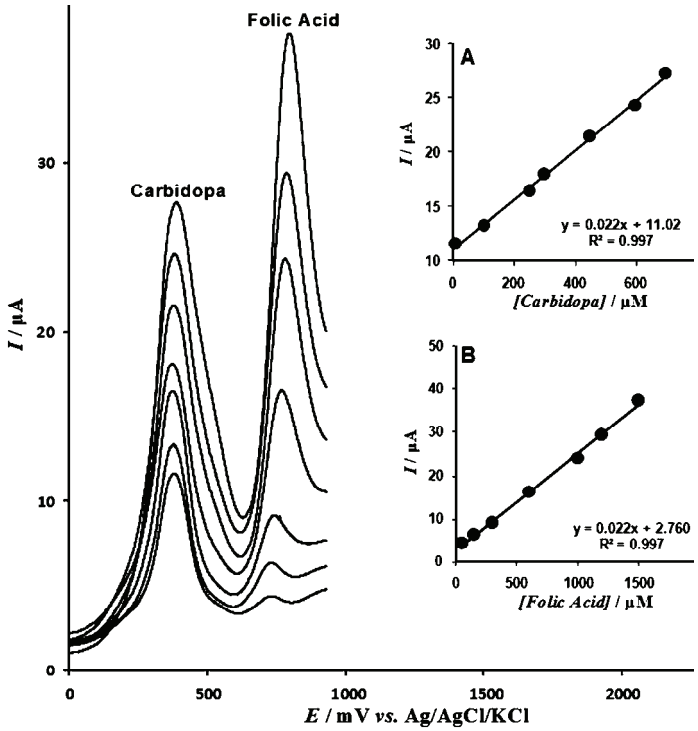

Fig.6. SWVs at the VFCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of carbidopa+folic acid in µM, from inner to outer: 10.0+50.0, 100.0+150.0, 250.0+300.0, 300.0+600.0, 450.0+1000.0, 600.0+1200.0 and 700.0+1500.0, respectively. Insets: plots of I_p *vs*. carbidopa (A) and folic acid concentration (B).

Determination of carbidopa and folic acid in urine sample

In order to evaluate the analytical applicability of the proposed method, it was also applied to the determination of carbidopa and folic acid in urine samples. The results for the determination of the carbidopa and folic acid in the urine samples are given in Table I. Satisfactory recovery was found for carbidopa

TABLE I. Determination of carbidopa and folic acid in urine samples. All the concentrations are given in µM (n = 5)

Carbidopa added, µM	Folic acid added µM	Carbidopa			Folic acid		
		Found µM	Recovery %	*RSD* %	Found µM	Recovery %	*RSD* %
0	0	ND	–	–	ND	–	–
15.0	5.0	15.3	102.0	2.9	5.3	106.0	2.4
25.0	10.0	24.6	98.4	1.8	9.9	99.0	3.1
35.0	15.0	34.1	97.4	1.9	15.1	100.7	2.2
45.0	20.0	45.1	100.2	2.3	20.2	101.0	2.8
55.0	25.0	54.8	99.6	2.6	25.6	102.4	1.7

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and folic acid. The reproducibility of the method was demonstrated by the mean relative standard deviation (*RSD*).

CONCLUSIONS

A novel modified carbon nanotube paste electrode was fabricated and applied to the determination of carbidopa and folic acid. The modified electrode showed excellent electrocatalytic activity for the oxidation of carbidopa and folic acid. Moreover, the modified electrode presented wide linear ranges, low detection limits and high stability for the simultaneous determination carbidopa and folic acid, suggesting this electrode as a good and attractive candidate for practical applications.

ИЗВОД

ВОЛТАМЕТРИЈСКО ОДРЕЂИВАЊЕ КАРБИДОПЕ И ФОЛНЕ КИСЕЛИНЕ КОРИШЋЕЊЕМ МОДИФИКОВАНЕ ЕЛЕКТРОДЕ ОД УГЉЕНИЧНЕ ПАСТЕ

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Развијен је нови електрохемијски сензор на бази угљеничне пасте модификоване угљеничним наноцевима и винил-фероценом са циљем селективне и осетљиве детекције карбидопе у присуству великог вишка фолне киселине у раствору физиолошке вредности pH. Велика сепарација струјних пикова, добра осетљивост и стабилност омогућавају да се помоћу ове електроде одреди концентрација карбидопе индивидуално и у присуству фолне киселине. Примењујући волтаметрију са правоугаоним сигналом, за карбидопу је добијен линеарни динамички опсег од $1{,}0\times10^{-6}$–$7{,}0\times10^{-4}$ M уз границу детекције $2{,}0\times10^{-7}$ M. Предложена метода примењена је и за одређивање карбидопе и фолне киселине у узорку урина.

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