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Nanostructured based Electrochemical Sensor for Voltammetric Determination of Ascorbic Acid in Pharmaceutical and Biological Samples

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Abstract- A novel carbon paste electrode modified with carbon nanotubes and 5-amino-2',4'-dimethoxy-biphenyl-2-ol (5ADMB) was fabricated. The electrochemical study of the modified electrode, as well as its efficiency for electrocatalytic oxidation of ascorbic acid, is described. Cyclic voltammetry was used to investigate the redox properties of this modified electrode at various scan rates. The apparent charge transfer rate constant, k_s, and transfer coefficient, α, for electron transfer between 5ADMB and carbon nanotubes paste electrode were calculated as 7.94 s^{-1} and 0.5, respectively. The electrode was also employed to study the electrocatalytic oxidation of ascorbic acid, using cyclic voltammetry, chronoamperometry

and square wave voltammetry as diagnostic techniques. It has been found that the oxidation of ascorbic acid at the surface of modified electrode occurs at a potential of about 250 mV less positive than that of an unmodified CPE. The diffusion coefficient, electron transfer coefficient, and heterogeneous rate constant, for oxidation of ascorbic acid at the modified electrode surface were also determined. Square wave voltammetry (SWV) exhibits a linear dynamic range from 1.0×10^{-6} to 7.5×10^{-4} M and a detection limit of 0.1 µM for ascorbic acid. Finally this modified electrode was used for determination of ascorbic acid in real samples.

Keywords- Ascorbic acid, Carbon nanotube paste electrode, Modified electrode, voltammetry

1. INTRODUCTION

Ascorbic acid is a water soluble vitamin with antioxidant properties. It is present in many biological systems and multivitamins preparations. One form of ascorbic acid is commonly known as vitamin C, which is an important vitamin for humans and animals. Ascorbic acid has an important role in formation of collagen and helps the absorption of iron via reduction [1]. It is commonly used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS [2]. Deficiency of ascorbic acid may cause anemia, weakness of capillary, deterioration in collagen, soft gums, wounds and skin hemorrhages. Furthermore, it may lower resistance to all infections and cause thyroid deficiency and premature ageing [1]. Nevertheless, excess of ascorbic acid can cause gastric irritation and diarrhea, giving as metabolic product oxalic acid, which can cause renal problems [3]. On the other hand, the concentration of ascorbic acid in foodstuffs, beverages, and pharmaceuticals can be an index of quality, since it varies during production and storage stages [1,4]. Therefore, the detection and determination of ascorbic acid is of great importance for pharmaceutical, clinical and food industry. Up to now, many methods have been used for the detection of ascorbic acid including spectroscopy [5], titrimitry [6], enzymatic analysis [7] and electrochemistry [8-16]. An important point is that ascorbic acid is electroactive at carbon and platinum electrodes. However, its oxidation requires undesirably high overvoltages. The latter is often confronted with electrode fouling, poor reproducibility, poor sensitivity and especially poor selectivity caused by the presence of other endogenous interferences such as uric acid, acetaminophen and dopamine, which are electroactive at high oxidation potentials. In order to improve the sensitivity and the selectivity of the detection of ascorbic acid, the operating potentials should be lowered and the oxidation currents should be increased. This can be achieved by modifying the surface of electrodes with suitable electrocatalysts.

Since the discovery of carbon nanotubes (CNTs) in 1991 [17], numerous investigations were focused on the studies of their properties and applications [18]. Because of the special tube structure, CNTs possess several unique properties such as good electrical conductivity, high chemical stability and extremely high mechanical strength [19]. In addition, the subtle electronic behavior of CNTs reveals that they have the ability to promote electron-transfer

reaction and have a high electrocatalytic effect when used as electrode materials [17-20]. All these fascinating properties make CNTs as a suitable candidate for the modification of electrodes [21-28].

The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amounts of biologically important compounds. One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decreasing of overpotential respect to unmodified electrode. With respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion, these electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [29-37].

Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrode consisting of mixture prepared from carbon powder (as graphite, glassy carbon and others carbonaceous materials) and a suitable water-immiscible or non-conducting binder [38, 39]. The use of carbon paste as an electrode was initially reported in 1958 by Adams [40]. In afterward researches a wide variety of modifiers including enzymes, polymers and nanomaterials have been used with these versatile electrodes. CPEs are widely applicable in both electrochemical studies and electroanalysis thank to their advantages such as very low background current (compared to solid graphite or noble metal electrodes), facility to prepare, low cost, large potential window, simple surface renewal process and easiness of miniaturization. Besides the advantageous properties and characteristics listed before, the feasibility of incorporation different substances during the paste preparation (which resulting in the so-called modified carbon paste electrode), allow the fabrication of electrodes with desired composition, and hence, with pre-determined properties [41-45].

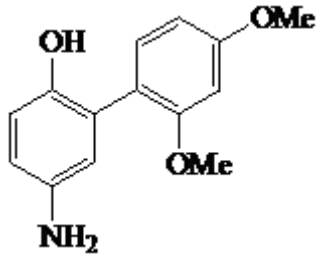
Therefore, in the present work, we describe the preparation of a new electrode composed of CNPE modified with 5-amino-2',4'-dimethoxy-biphenyl-2-ol (5ADMBCNPE) and investigate its performance for the electrocatalytic determination of ascorbic acid in aqueous solutions.

2. EXPERIMANTAL

2.1. 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 (5ADMBCNPE) 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. Ascorbic acid and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Graphite powder and paraffin oil (DC 350, density=0.88 g cm^{-3}) as the 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 from Nanostructured & Amorphous Materials, Inc. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0-11.0. 5ADMB (Scheme 1) was synthesized in our laboratory as reported previously [32].



Scheme 1. Structure of 5ADMB

2.2. Preparation of the electrode

The 5ADMBCNPEs were prepared by hand mixing 0.01 g of 5ADMB with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~ 0.7 mL of paraffin oil was added to the above 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, 5ADMB modified CPE electrode (5ADMBCPE) without CNTs, CNTs paste electrode (CNPE) without 5ADMB, and unmodified CPE in the absence of both 5ADMB and CNTs were also prepared in the same way.

2.3. Procedure of real samples preparation

One milliliter of an ascorbic acid ampoule (Darou Pakhsh, Iran) was diluted to 10 mL with 0.1 M PBS (pH 7.0); then, different volume of the diluted solution was transferred into each of a series of 25 mL volumetric flasks and diluted to the mark with PBS. The ascorbic acid content was analyzed by the proposed method using the standard addition method.

The multivitamine syrup solution (Darou Pakhsh, Iran) was diluted 1000 times with deionized water; then, different volume of the diluted solution was transferred into a 25 mL

volumetric flask and diluted to the mark with PBS (pH 7.0). The ascorbic acid content was analyzed by the proposed method using the standard addition method.

Effervescent tablet solution was prepared by completely grinding and homogenizing 10 tablets, labelled 1000 mg per tablet (Darou Pakhsh, Iran). Then, 10 mg of each tablet powder was accurately weighed and dissolved in 100 ml water by ultrasonication. Different volume of the diluted solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The ascorbic acid content was analyzed by the proposed method using the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of 5ADMBCNPE

5ADMBCNPEs were prepared and their electrochemical properties were studied in a buffered aqueous solution (pH 7.0) using CV (Fig.1). It should be noted that one of the advantages of 5ADMB as an electrode modifier is its insolubility in aqueous media. Experimental results showed reproducible, well-defined, anodic and cathodic peaks with E_{pa}, E_{pc} and E°´ of 0.29, 0.17 and 0.23 V *vs.* Ag/AgCl/KCl (3.0 M) respectively. The observed peak separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 120 mV, was greater than the value of 59/n mV expected for a reversible system [46], suggesting that the redox couple of 5ADMB in 5ADMBCNPE has a quasi-reversible behavior in aqueous medium. The effect of the potential scan rate (ν) on electrochemical properties of the 5ADMBCNPE was also studied by CV. Plots of the both anodic and cathodic peak currents (I_p) were linearly dependent on ν in the range of 10 to 800 mV s^{-1} (Fig. 1A), indicating that the redox process of 5ADMB at the modified electrode is diffusionless in nature.

The apparent charge transfer rate constant, k_s, and the charge transfer coefficient, α, of a surface-confined redox couple can be evaluated from CV experiments by using the variation of anodic and cathodic peak potentials with logarithm of scan rate, according to the procedure of Laviron [47]. Fig. 1B shows such plots, indicating that the E_p values are proportional to the logarithm of scan rate for ν values higher than 2 Vs^{-1} (Fig. 1B). The slopes of the plots in Fig. 1B can be used to extract the kinetic parameters α_c and α_a (cathodic and anodic transfer coefficients, respectively). The slope of the linear segments are equal to $-2.303RT/\alpha nF$ and $2.303RT/(1 - \alpha) nF$ for the cathodic and anodic peaks, respectively. The evaluated value for the α is 0.5.

Also, Eq. 1 can be used to determine the electron transfer rate constant between modifier (5ADMB) and CNPE:

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nF\nu) - \alpha (1-\alpha) nF\Delta E_p/2.3RT \quad (1)$$

where $(1-\alpha)n_\alpha = 0.5$, ν is the sweep rate and all other symbols having their conventional meanings. The value of k_s was evaluated to be 7.94 s^{-1} using Eq. (1).

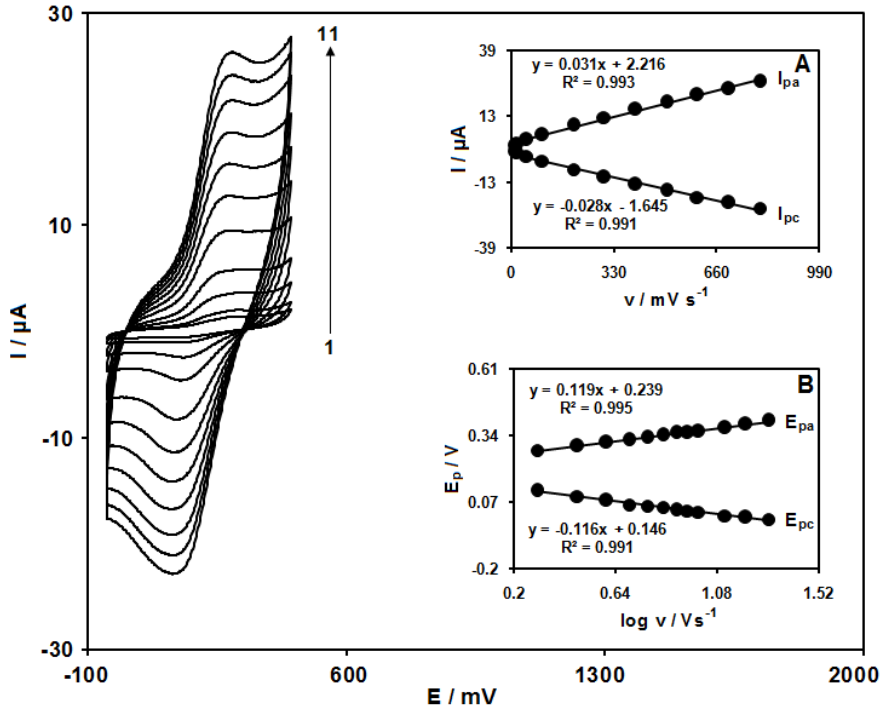


Fig. 1. CVs of 5ADMBCNPE in 0.1 M PBS (pH 7.0), at various scan rates, numbers 1-11 correspond to 10, 20, 50, 100, 200, 300, 400, 500, 600, 700 and 800 mVs^{-1}. Insets: variation of **(A)** I_p *vs*. scan rate; **(B)** Variation of E_p versus the logarithm of the high scan rates

3.2. Influence of pH

The electrochemistry of 5ADMB molecule is generally pH dependent. Thus, the electrochemical behavior of 5ADMBCNPE was studied at different pHs using SWV (Fig. 2). It was observed that the anodic and cathodic peak potentials of 5ADMBCNPE shift to less positive values with increasing pH. Inset of Fig. 2 shows potential-pH diagrams constructed by plotting the anodic potential values as the function of pH. As can be seen the slope is 50.0 mV/pH for E_p, indicating that the system obeys the Nernst equation for an equal electron and proton transfer reaction [46].

3.3. Electrocatalytic oxidation of ascorbic acid at a 5ADMBCNPE

Fig. 3 depicts the CV responses for the electrochemical oxidation of 0.1 mM ascorbic acid at unmodified CPE (curve b), CNPE (curve d), 5ADMBCPE (curve e) and 5ADMBCNPE (curve f). As it is seen, while the anodic peak potential for ascorbic acid oxidation at the CNPE, and unmodified CPE are 490 and 540 mV, respectively, the corresponding potential at 5ADMBCNPE and 5ADMBCPE is ~290 mV. These results indicate that the peak potential for ascorbic acid oxidation at the 5ADMBCNPE and

5ADMBCPE electrodes shift by ~200 and 250 mV toward negative values compared to CNPE and unmodified CPE, respectively. However, 5ADMBCNPE shows much higher anodic peak current for the oxidation of ascorbic acid compared to 5ADMBCPE, indicating that the combination of CNTs and the mediator (5ADMB) has significantly improved the performance of the electrode toward ascorbic acid oxidation. In fact, 5ADMBCNPE in the absence of ascorbic acid exhibited a well-behaved redox reaction (Fig. 3, 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 0.1 mM ascorbic acid (curve f), which can be related to the strong electrocatalytic effect of the 5ADMBCNPE towards this compound [46].

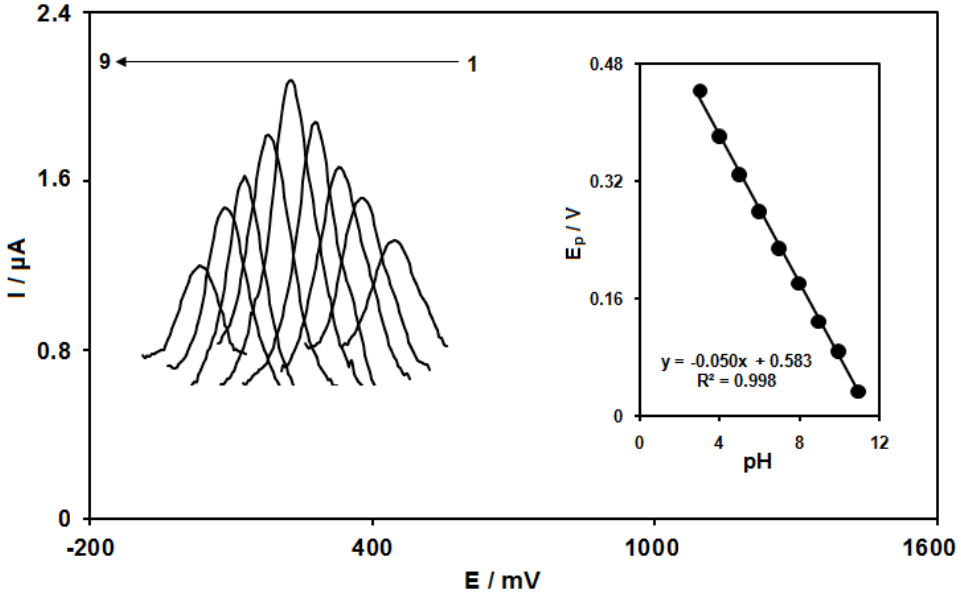


Fig. 2. SWVs (at 20 mV s^{-1}) of 5ADMBCNPE at various buffered pHs. The numbers 1–9 correspond to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0 pHs, respectively. Inset: Plot of E_p *vs*. pH

The effect of scan rate on the electrocatalytic oxidation of ascorbic acid at the 5ADMBCNPE was investigated by linear sweep voltammetry (LSV) (Fig. 4). As can be observed in Fig. 4, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) *vs*. the square root of scan rate ($v^{1/2}$) was found to be linear in the range of 2-50 mVs^{-1}, suggesting that, at sufficient overpotential, the process is diffusion rather than surface controlled (Fig. 4A) [46]. A plot of the scan rate-normalized current ($I_p/v^{1/2}$) *vs*. scan rate (Fig. 4B) exhibits the characteristic shape typical of an EC′process [46].

The Tafel slope (b) can be obtained from the slope of E_p *vs*. log v using Eq. (2) [46]:

$$Ep = b/2 \log v + constant \quad (2)$$

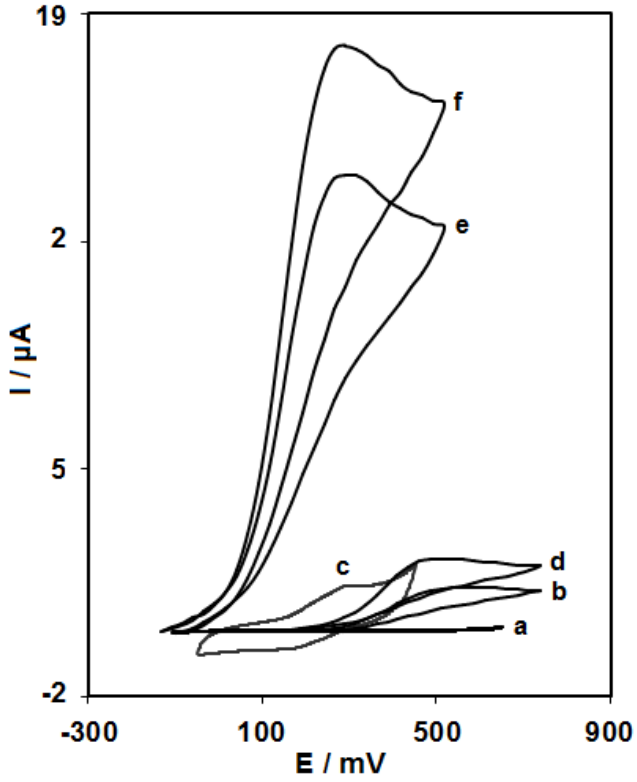


Fig. 3. CVs of (a) unmodified CPE in 0.1 M PBS (pH 7.0), (b) unmodified CPE in 0.1 mM ascorbic acid, (c) 5ADMBCNPE in 0.1 M PBS, (d) CNPE in 0.1 mM ascorbic acid, (e) 5ADMBCPE in 0.1 mM ascorbic acid, and (f) 5ADMBCNPE in 0.1 mM ascorbic acid. In all cases the scan rate was 10 mVs^{-1}

The Tafel slope was found to be 84 mV (Fig. 4, inset C), which indicates that a one-electron transfer process is the rate limiting step assuming a transfer coefficient (α) is about 0.3.

3.4. Chronoamperometric measurements

Chronoamperometric measurements of ascorbic acid at 5ADMBCNPE were carried out by setting the working electrode potential at 0.35 V *vs*. Ag/AgCl/KCl (3.0 M) for the various concentration of ascorbic acid in PBS (pH 7.0) (Not shown). For an electroactive material (ascorbic acid in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [46]. Experimental plots of I *vs.* $t^{-1/2}$ were employed, with the best fits for different concentrations of ascorbic acid. The slopes of the resulting straight lines were then plotted *vs.* ascorbic acid concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be 6.7×10^{-6} cm^2 s^{-1}.

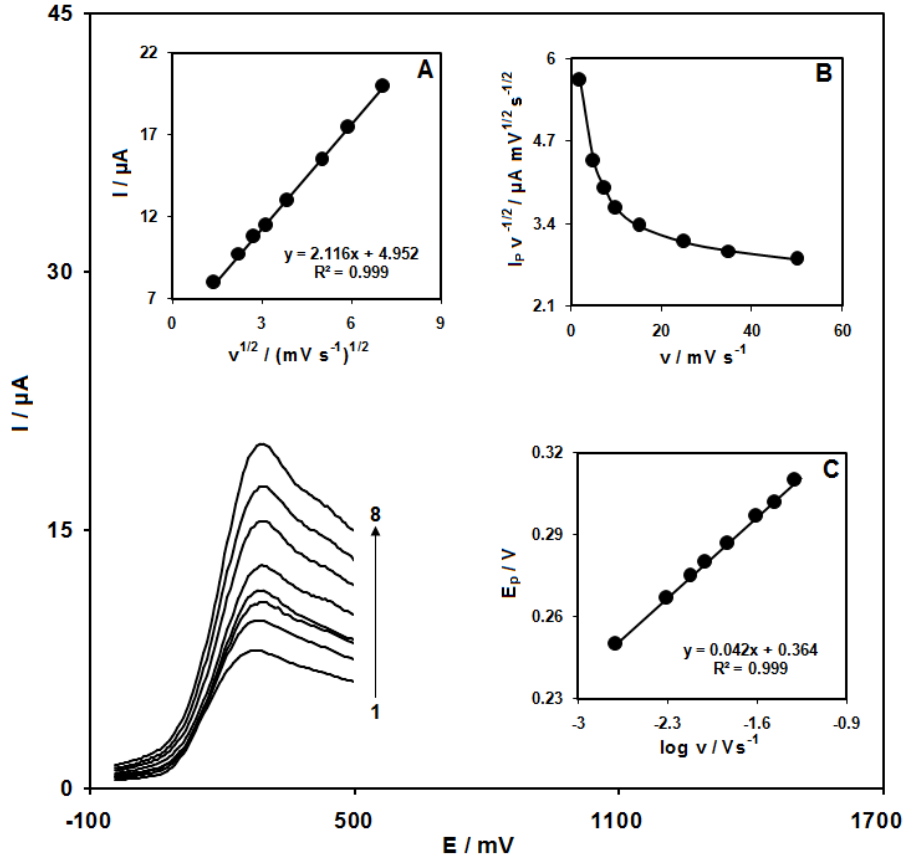


Fig. 4. LSVs of 5ADMBCNPE in 0.1 M PBS (pH 7.0) containing 50.0 µM ascorbic acid at various scan rates; numbers 1-8 correspond to 2, 5, 7.5, 10, 15, 25, 35 and 50 mVs^{-1}, respectively. Insets: Variation of **(A)** anodic peak current *vs.* $v^{1/2}$; **(B)** normalized current ($I_p/v^{1/2}$) *vs.* v; **(C)** anodic peak potential *vs.* log v

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k, for the reaction between ascorbic acid and the 5ADMBCNPE according to the method of Galus [48]:

$$I_C / I_L = \gamma^{1/2}[\pi^{1/2} \text{ erf } (\gamma^{1/2}) + \exp(-\gamma) / \gamma^{1/2}] \quad (3)$$

Where I_C is the catalytic current of ascorbic acid at the 5ADMBCNPE, I_L is the limited current in the absence of ascorbic acid and $\gamma = kC_bt$ is the argument of the error function (C_b is the bulk concentration of ascorbic acid). In cases where γ exceeds the value of 2, the error function is almost equal to 1 and therefore, the above equation can be reduced to:

$$I_C / I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_bt)^{1/2} \quad (4)$$

Where t is the time elapsed. The above equation can be used to calculate the rate constant, k, of the catalytic process from the slope of I_C/I_L *vs.* $t^{1/2}$ at a given ascorbic acid concentration. From the values of the slopes, the average value of k was found to be 4.6×10^{4} M^{-1} s^{-1}.

3.5. Electrocatalytic Determination of ascorbic acid

SWV method was used to determine the concentration of ascorbic acid (Fig.5). The plot of peak current *vs.* ascorbic acid concentration consisted of two linear segments with slopes of 0.141 and 0.049 μA μM^{-1} in the concentration ranges of 1.0 to 50.0 μM and 50.0 to 750.0 μM, respectively. The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation [46]. The detection limit (3σ) of ascorbic acid was found to be 0.1 μM.

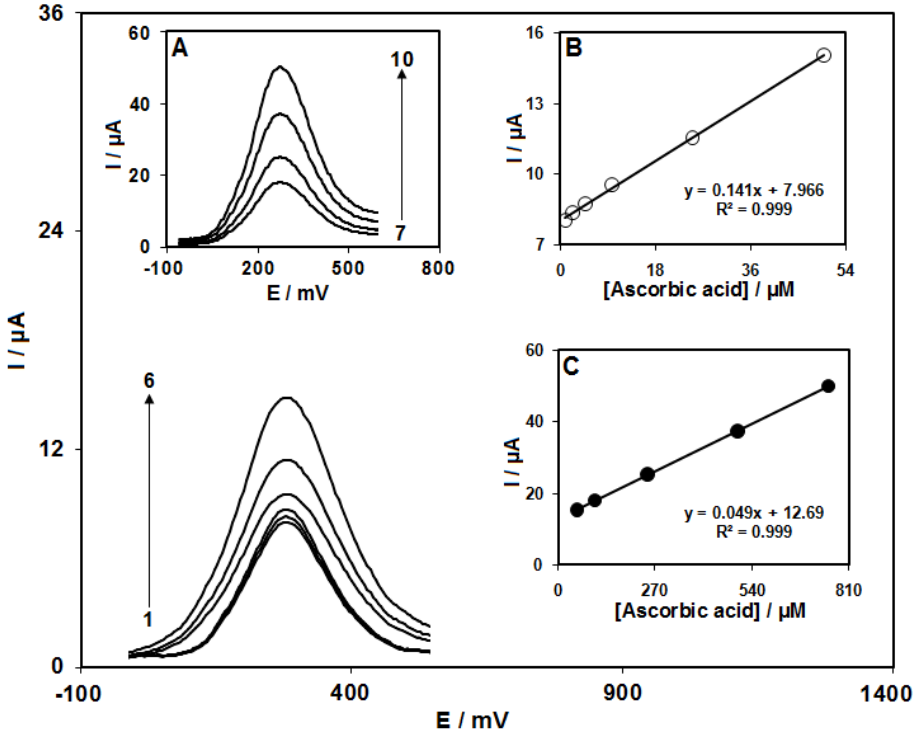


Fig. 5. SWVs of 5ADMBCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of ascorbic acid. Numbers 1-10 correspond to 1.0, 2.5, 5.0, 10.0, 25.0, 50.0, 100.0, 250.0, 500.0 and 750.0 μM of ascorbic acid. Inset show the plots of the electrocatalytic peak current as a function of ascorbic acid concentration in the ranges of **(B)** 1.0-50.0 μM and **(C)** 50.0-750.0 μM

3.6. Determination of AA in pharmaceutical sample

The proposed 5ADMBCNPE was found to work well under laboratory conditions. The electrode was also successfully applied to the direct determination of ascorbic acid content of pharmaceutical samples. The ascorbic acid content in pharmaceutical samples was determined by the standard addition method in order to prevent of any matrix effect. The results for the analysis of pharmaceutical samples with the voltammetric method compared favorably with those obtained by the USP standard method (Table 1).

For titration method, a 0.05 M iodone solution was standardized in the usual way with a primary standard of As_2O_3 or titrisol thiosulfate solution. For a pharmaceutical analysis, an iodometric procedure, described in the US pharmacopeia (USP), was used [49].

Table 1. Determination of AA in real samples

Pharmaceutical preparation	Claimed (mg)	Proposed method [a] (mg)(%RSD)	Iodine method[a] (mg)(%RSD)	$F_{exp.}$	$T_{exp.}$
Effervescent tablet	1000 per tablet	990.0 (0.4)	985.0 (0.3)	1.7	0.9
Ampoule	500 per 5 ml	508.0 (0.3)	494.0 (0.5)	1.1	1.3
Multivitamine syrup	60 per 5 ml	60.5 (1.3)	58.9 (1.6)	2.2	1.1

[a] Result based on five replicate determinations per samples. Theoretical values for t=2.31 and F=6.39 (p=0.05)

4. CONCLUSION

The 5ADMBCNPE was prepared and used for the investigation of the electrochemical behavior of ascorbic acid. Two pairs of well-defined redox peaks were obtained at the 5ADMBCNPE. The 5ADMBCNPE showed excellent electrocatalytic activity for the ascorbic acid. The SWV currents of ascorbic acid at 5ADMBCNPE increased linearly with the ascorbic acid concentration in the range from 1.0 to 750.0 μM with a detection limit of 0.1 μM. Finally, this method was used for the determination of ascorbic acid in some real samples.

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