

Full Paper

Voltammetric Determination of Folic acid in presence of Dopamine and Ascorbic Acid at Poly (Alanine) Modified Carbon Paste Electrode

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Abstract- A procedure for the electropolymerization of alanine on the surface of bare carbon paste electrode (CPE) in presence 0.2 M acetate buffer (pH 5.0) solution as a supporting electrolyte using cyclic voltammetric technique was developed. The optimization of electropolymerized modified carbon paste electrode (MCPE) was achieved at 25 cycles. Further the poly (alanine) MCPE was used for the electrochemical detection for the folic acid (FA) at pH 5.0 and shows excellent electrocatalytic activity towards FA when compared to the bare CPE. The various parameters such as effect of scan rate, concentration of FA and the effect of pH were studied at MCPE. From the scan rate it was found that the electrode process was adsorption-controlled process. The limit of detection of FA was calculated at MCPE and the simultaneous determination FA, DA and AA shows three well defined oxidation peaks at poly (alanine) MCPE.

Keywords- Eletropolymerisation, Folic acid, Dopamine, Ascorbic acid, DL-alanine, Cyclic voltammetry

1. INTRODUCTION

Electrochemical sensors have found wide applications in critical care, safety issues, and industrial hygiene as well as in process and quality control. The principle of electrochemical sensors is based on the fact the current generated by the oxidation or reduction of an electroactive analyte on the working electrode surface is measured by the electrochemical detector within a specified fixed or varying potential. The instruments used for electrochemical detection are simple to construct, cheap, and miniaturizable [1,2,3].

Folic acid, N-[p-[(2-amino-4-hydroxy-6-pteridiny) methyl]amino}benzoyl]-L-glutamic acid often regarded as a part of vitamin B complex, possesses the considerable biological importance for general human health, especially during periods of rapid cell division and growth. The structure of folic acid (FA) was shown in Scheme 1. The deficiency of FA will cause serious diseases, notably for women planning for pregnancy, which can result in malformations of the spine, skull, and brain. Therefore, the determination of FA has drawn significant attention, and a reliable and sensitive detection method is highly expected. At present, some measurements, such as spectrophotometry, fluorometric high-performance liquid chromatography (HPLC) and flow injection chemiluminescence have been used to detect FA. However, these techniques are complex, time-consuming, and require expensive instruments. Electrochemical methods have also been used and attracted enormous interest due to its advantages of simplicity, rapid response, excellent reproducibility, good stability, low cost and low detection limit, etc. [4-16].

Dopamine (DA) and ascorbic acid (AA) are compounds of great biomedical and neurochemical interest playing a potential role in human metabolism. DA is one of the most significant catecholamine, functioning as a neurotransmitter in the central nervous system and a medicament to drug addiction and Parkinson's disease. AA has been used in the prevention and treatment of common cold, mental illness, cancer and Aids. In mammalian brain DA and AA coexists in the extracellular fluids. Thus the simultaneous determination of DA and AA is of critical importance in the field of biochemistry and medical treatment. Among various determination methods includes ultraviolet spectroscopy (UV), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). Electrochemical approaches have obtained considerable attention for their high sensitivity and selectivity, especially for the in-vivo detection of neurotransmitter [17-28].

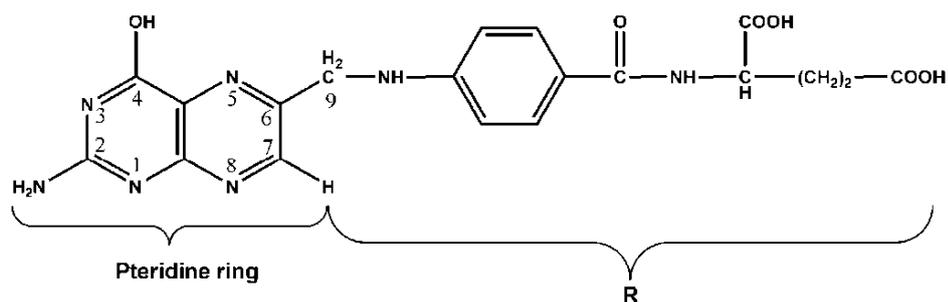
Carbon paste electrode was very much attracted towards the determination of biologically active molecules because of the easy preparation of modified electrode, renewability, and low background current and fast response. A number of modified electrodes were developed by using carbon paste, glassy carbon, polymer, metal oxides and nonmaterial's for the determination of DA by using voltammetric techniques [29-34]. Similarly, Vitamin C (L-ascorbic acid), a water-soluble vitamin that is widely required for metabolism and consumed on a large scale, is electroactive and has been studied extensively [35-39]. Because AA exist

at much higher concentration than that of DA and oxidizes at a near potential with DA on bare carbon electrode surface which result in an overlap of their voltammetric response [40, 41] AA has been used for the prevention and treatment of common cold, mental illness, infertility, cancer and AIDS. Up to now, the ability to detect DA with high selectivity and sensitivity is still a major target of electroanalytical research [42-45].

Polymer film, which can be easily deposited onto the surface of the electrode by electro polymerization, has significant advantages including easier fabrication process, more excellent electrochemical catalytic ability, better physical stability over composites as modifier[46].

Polymer modified electrodes (PMEs) have received great attention in recent years, as the polymer film have good stability, reproducibility, more active sites, homogeneity in electrochemical deposition and strong adherence to the electrode surface [47,48]. Electropolymerisation is a good approach to immobilize polymers to prepare PME. Carbon based electrodes have been used. Among them, glassy carbon electrodes (GCEs) have been widely used compared to metal electrodes due to its biocompatibility, having low residual current over a wide range and having minimal chances to show deteriorated response as a result of electrode fouling [49-51].

The present work describes an electropolymerisation film of DL-alanine on the surface of carbon paste electrode by cyclic Voltammetric technique. On the basis of its different electrochemical behavior the poly (alanine) MCPE was used for the detection of electroactive molecules like, dopamine, ascorbic acid, uric acid, noradrenaline, etc. Thus the present study provides a novel method for selective and sensitive detection of FA in the presence of DA & AA, which has a significant attraction in biological and chemical fields.



Scheme 1. Structure of folic acid

2. EXPERIMENTAL PART

2.1. Reagents

Folic acid was purchased from Sigma Aldrich and its stock solution was prepared by diluted NaOH aqueous solution, Dopamine hydrochloride and NaOH were purchased from nice chemicals. Ascorbic acid from sd. fine chemical laboratory, DL-alanine from Himedia. The chemicals for the preparation of buffer solution were purchased from Merck. The acetate buffer solution (ABS) used as supporting electrolyte and was prepared by mixing standard stock solutions of 0.2 M CH_3COOH and CH_3COONa and adjusting the pH with 0.2 M CH_3COOH or 0.2 M NaOH. Freshly prepared solutions of FA, DA, and AA were prepared at the time of experiments. All the aqueous solutions were prepared using double distilled water.

2.2. Apparatus

Cyclic voltammetry was performed with EA-201 Electroanalyser working station controlled by a personal computer. A conventional three electrode electrochemical cell contained a bare CPE or poly(alanine) modified CPE as working electrode, platinum wire counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The pH values were measured with a digital pH meter MK VI (systronics).

2.3. Preparation of bare carbon paste electrode

The bare CPE was prepared by hand mixing of graphite powder and silicon oil at a ratio 70:30 in an agate mortar until a homogenous paste was obtained. The paste was then tightly packed into a PVC tube (3mm internal diameter) and the electrical contact was provided by a copper wire connected to the end of the tube.

2.4. Preparation of poly (alanine) modified electrode

The paste packing procedure was same as that at the bare carbon paste electrode. Electrochemical polymerization of DL-alanine at the carbon paste electrode was done by using cyclic voltammetric method in aqueous solution containing 1 mM alanine in 0.2 M acetate buffer solution at pH 5.0. Electropolymerisation was achieved by the formation of film that grew between 100 mV s^{-1} to 1400 mVs^{-1} at a scan rate of 50 mV s^{-1} for 25 cycles using cyclic voltammetry.

3. RESULTS AND DISCUSSION

3.1. Electropolymerisation of DL-alanine at the surface of carbon paste electrode

The electropolymerisation of DL-alanine on the surface of carbon paste electrode was investigated by cyclic voltammetry, which is shown in Fig. 1. The potential scan range

especially the positive potential, was the most important factor for preparing the polymer film. If positive potential value for polymerization was below 1000 mV s^{-1} or negative one was above -100 mV there was no polymer formation on the surface of the electrode. When the positive potential value reached 1200 mVs^{-1} the electropolymerisation was observed. The experimental results showed that a better conductive polymeric film could be formed when potential scan window was from -100 mV to 1400 mV . Therefore we selected it for electropolymerisation potential window in this work. The plot of I_{pa} versus number of cycles on the electrocatalytic oxidation peak current (I_{pa}) of $0.1 \times 10^{-4} \text{ M}$ FA in 0.2 M acetate buffer at pH 5.0 as shown in the Fig. 2. The anodic peak current response shows maximum up to 25 cycles and decreases thereafter. This may be due to the increase in the surface coverage of the electrode with poly (alanine) with increasing the number of cycles.

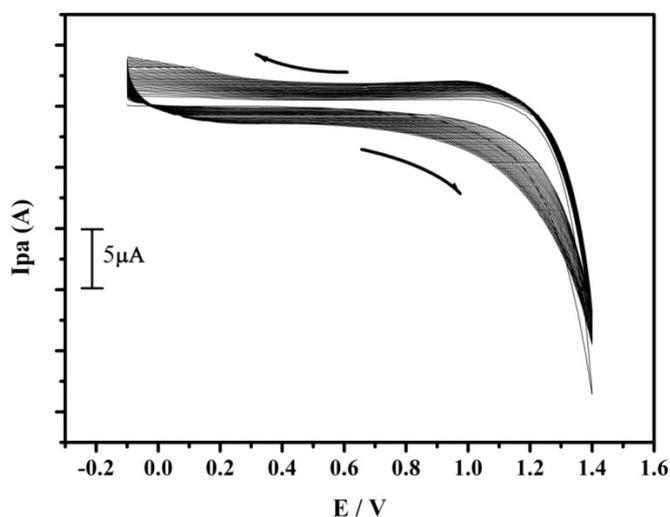


Fig. 1. Cyclic voltammogram for the electrochemical polymerization of 1 mM DL-alanine recorded with bare CPE in 0.2 M ABS (pH5.0) scan rate 50 mVs^{-1}

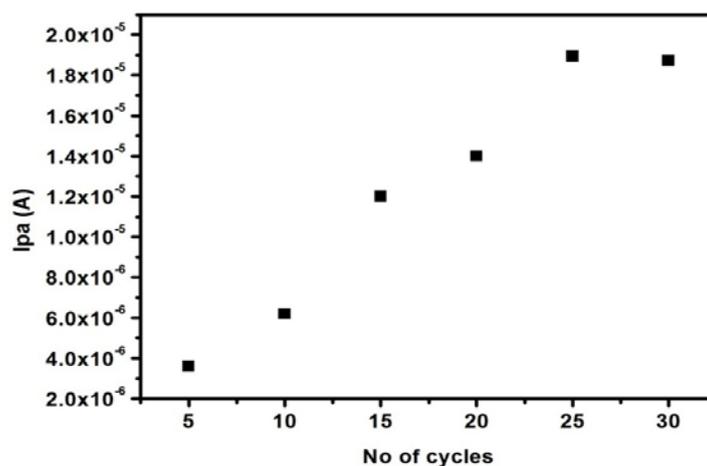


Fig. 2. Plot of Anodic peak current versus number of cycles

3.2. Electrochemical oxidation of FA at the poly (alanine) MCPE

Fig. 3 shows the cyclic voltammogram of 0.1×10^{-4} M FA at the bare CPE (solid line curve) and poly(alanine) MCPE (dashed line curve) in 0.2 M acetate buffer solution (ABS) pH 5.0 recorded at the scan rate 50 mVs^{-1} . At the bare CPE the oxidation peak potential was found by 0.70 V and oxidation peak current was 2.5×10^{-6} A. However at the poly (alanine) MCPE, the oxidation peak potential of FA was obtained at around 0.836 V and oxidation peak current was 1.0×10^{-5} A. The poly(alanine) MCPE shows enhancement in anodic peak current when compare to BCPE confirming that poly(alanine) MCPE shows significance increase in the current signal than BCPE. This indicates that poly (alanine) MCPE shows good electrocatalytic activity towards FA.

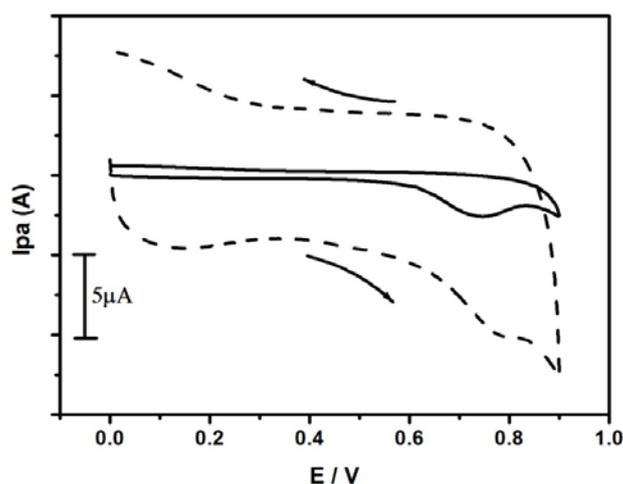


Fig. 3. Cyclic voltammograms obtained for the oxidation of 0.1×10^{-4} M FA folic acid at poly (alanine) modified electrode (dashed line curve) and bare CPE (solid line curve) in 0.2 M ABS (pH5.0) scan rate 50 mVs^{-1}

3.3. The effect of scan rate on poly (alanine) MCPE

Fig. 4a shows the cyclic voltammograms of 0.1×10^{-4} M FA on Poly (alanine) MCPE at different scan rate from 50 – 500 mVs^{-1} , with the increase of the scan rate, the anodic peak currents also increased gradually. Fig. 4b shows the graph of anodic peak current (I_{pa}) versus scan rate (ν), shows linear relationship with correlation coefficient ($R^2=0.999$) which indicates the electrode reaction was adsorption controlled.

3.4. The effect of concentration on poly (alanine) MCPE

Fig. 5a shows the cyclic voltammograms of different concentrations of folic acid in 0.2 M ABS pH 5.0 at a scan rate of 50 Vs^{-1} at Poly (alanine) MCPE. The anodic peak current

slightly shifting towards positive values while increasing the concentration of FA in the range $(0.1-0.8 \times 10^{-4} \text{ M})$. Fig. 5b shows the plot of I_{pa} versus concentration of FA show two correlation coefficient for first linearity was 0.99743 and for second it was found to be 0.98672. The decrease of sensitivity in second linear range is likely to be due to the kinetic limitation. The detection limits was calculated by using the formula (1), where S is the standard deviation and M is the slope obtained from the calibration plots [52]. The detection limit for first linear range (A) was found to be $3.407 \times 10^{-6} \text{ M}$ and second linear range (B) was found to be $0.780 \times 10^{-6} \text{ M}$ and it was compared in the Table 1.

$$\text{LOD} = 3S/M \quad (1)$$

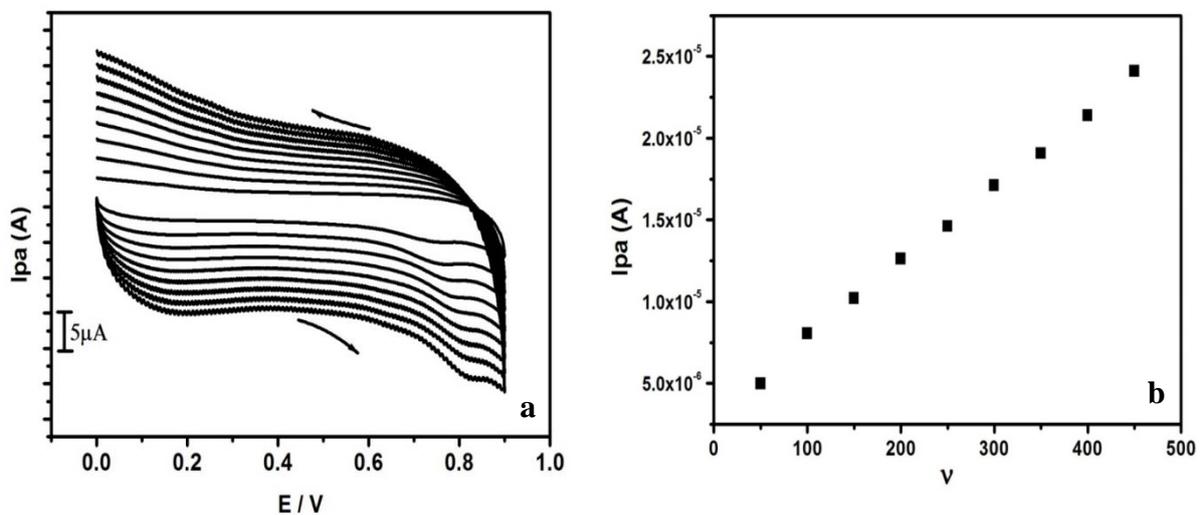


Fig. 4. a) Cyclic voltammograms of $0.1 \times 10^{-4} \text{ M}$ FA on the Poly (alanine) modified CPE at different scan rates ($50-500 \text{ mVs}^{-1}$) in 0.2 M ABS (pH5.0) and **b)** the plot of the anodic peak current versus scan rate

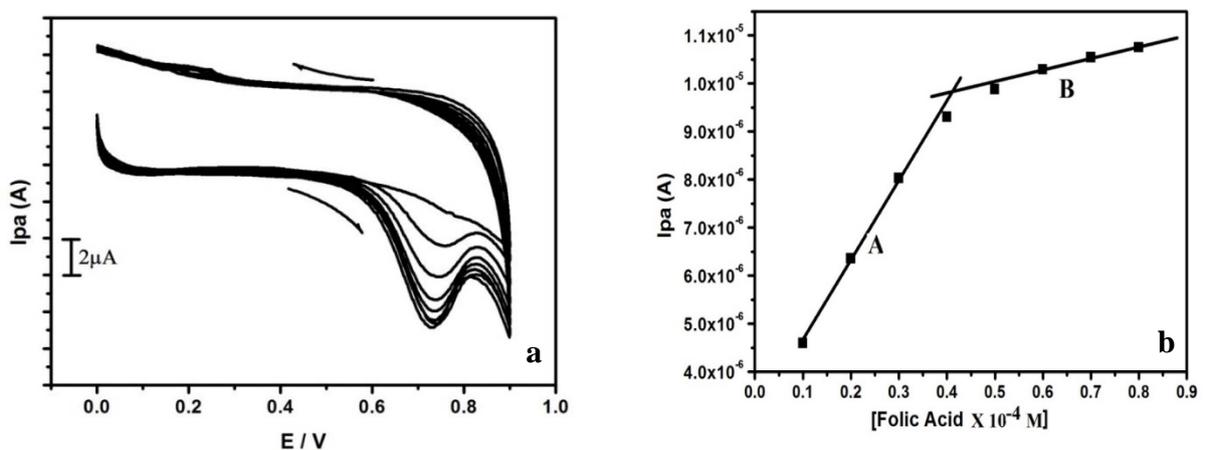


Fig. 5. a) Cyclic voltammograms of different concentration ($0.1-0.8 \times 10^{-4} \text{ M}$) of FA at poly(alanine) modified CPE in 0.2 M ABS (pH 5.0) at scan rates 50 mVs^{-1} and **b)** the plot of the anodic peak current versus concentration of FA

Table 1. Comparison of the present work with previous reported ones

Modified electrodes	Method	Detection Limit (μM)	Linear range (μM)	Ref.
$\alpha\text{-Fe}_2\text{O}_3$ nanofibers/GCE	i-t curve	0.00011	0.06–60	[55]
DNA/PGE	DPV	0.0106	0.1–10	[56]
ZrO ₂ nanoparticles/CPE	DPV	0.089	10–2000	[57]
P-AMT/GCE	i-t curve	0.00023	0.1–800	[58]
Ni-POA/CPE	CV	91	100–5000	[59]
Poly(Alanine) MCPE	CV	A: 3.40 B: 0.780	10- 40 50-80	Present Work

3.5. The effect of pH on poly (alanine) MCPE

Cyclic voltammetry was used to investigate the effects of pH value in the determination of FA at Poly (alanine) modified CPE. Fig. 6a shows cyclic voltammograms obtained at poly (alanine) modified CPE in 0.2 M Acetate buffer solutions of different pH values containing 0.1 mM FA at scan rates of 50 mVs⁻¹.

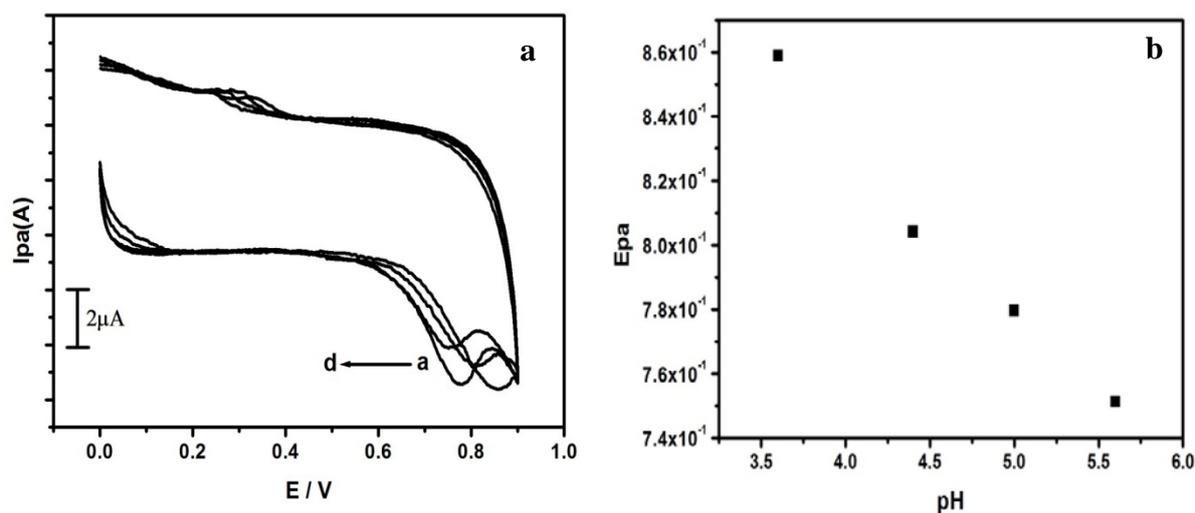


Fig. 6. a) Cyclic voltammograms obtained at Poly (alanine) modified CPE in 0.2 M ABS (pH 5.0) in pH values(3.6, 4.4, 5.0,5.6) containing 0.1×10^{-4} FA at scan rate 50 mVs⁻¹; **b)** the plot of the anodic peak potential versus pH

As illustrated in (Fig. 6b) the anodic peak current was shifted to a less positive potential with increase of pH values .Because the negative carboxylic group on the electrode surface is

increased on increasing the pH. So more FA cations are attracted towards the electrode surface. Hence, the oxidation potential of FA were shifted to less positive values. The influence of pH on the oxidation potential of FA was also investigated (Fig. 6b). In the pH range from 3.6 to 5.6 the standard potential E^0 decreases with increase of pH, the graph has good linearity with a slope of 51 mV/pH, this behavior is nearly obeyed the Nernst Equation for two electron and two proton transfer reaction [53,54].

3.6. Simultaneous detection of FA in the presence of DA and AA at poly (alanine) MCPE

The main objective of the present work was the determination of DA, AA & FA in ABS. The Fig. 7 shows the cyclic voltammograms of simultaneous study of 0.5×10^{-4} M DA, 2×10^{-4} M AA and 0.1×10^{-4} M FA at pH 5.0 ABS. At bare CPE (dotted line) the oxidation pH of DA, AA & FA was unable to separate. However at poly (alanine) MCPE (solid line) shows well defined oxidation peak of DA, AA & FA at 0.307 mV, 0.026 mV and 0.744 mV respectively. This indicates that MCPE act as a good electrochemical sensor for the determination of DA, AA & FA.

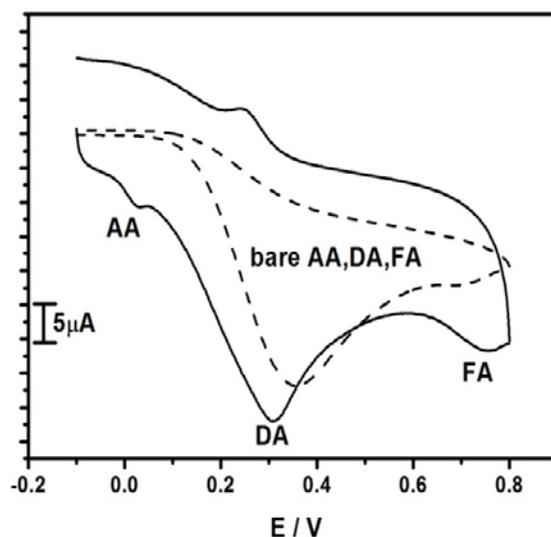


Fig. 7. Cyclic voltammograms obtained for oxidation of DA, AA, and FA at bare (dashed line) and Poly (alanine) MCPE (solid line) at scan rate of 100 mVs^{-1} 0.2 M ABS (pH5.0)

Differential pulse voltammogram was used for the determination of for 0.5×10^{-4} M DA, 2×10^{-4} M AA and 0.1×10^{-4} M FA because it has more sensitivity and selectivity the simultaneous study was carried out in the potential range from -0.2 to 1.0 at pH 5.0 (Fig. 8) and DPV shows three well defined oxidation peaks at Poly (alanine) MCPE. The oxidation peak potential of DA, AA, and FA were 0.264 mV, 0.0038 mV and 70.6 mV, respectively.

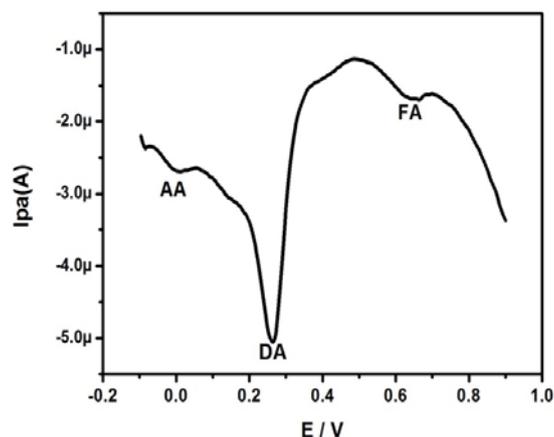


Fig. 8. Differential pulse voltammogram for DA 0.5×10^{-4} M, AA 2×10^{-4} M and for FA 0.1×10^{-4} M at poly (alanine) modified carbon paste electrode at 50 mVs^{-1}

4. CONCLUSION

In this work, the CPE was modified with alanine by electropolymerisation technique and was used for the electrochemical determination of DA, AA, and FA. The results also indicated that the problem of the overlapped voltammetric responses of DA with AA, due to their coexistence in real biological matrix can be effectively overcome by use of poly (alanine) MCPE. Poly (alanine) MCPE showed excellent high sensitive current has been proved to be efficient for the electrocatalytic activity oxidation of Folic acid. Because of its high electrocatalytic behavior, good selectivity, sensitivity and reproducibility. Therefore the poly (alanine) modified carbon paste electrode shows good application in the field of electroanalytical chemistry.

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