

*Full Paper*

## **Poly(maleic acid) Modified Carbon Paste Electrode for Simultaneous Detection of Dopamine in the Presence of Uric Acid : A Cyclic Voltammetric Study**

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**Abstract-** A voltammetric method using a poly(maleic acid) modified carbon paste electrode was developed for the quantification of dopamine. The modified electrode exhibited stable and sensitive current responses towards dopamine and potassium ferrocyanide. Compared with a bare CPE, the modified electrode exhibits a remarkable shift of the oxidation potentials of dopamine in the cathodic direction and a drastic enhancement of the anodic current response. The separation between anodic and cathodic peak potentials for dopamine is 0.84 V in 0.2 M phosphate buffer solution (PBS) at pH 7.0 at modified carbon paste electrodes. The poly (maleic acid) CPE was also effective to simultaneously determine dopamine and uric acid in a mixture and resolved the overlapping anodic peaks of these two species into two well-defined voltammetric peaks in cyclic voltammetry. The proposed method showed excellent stability and reproducibility.

**Keywords-** Poly(maleic acid), Dopamine, Uric Acid, Electropolymerisation, Cyclic Voltammetry

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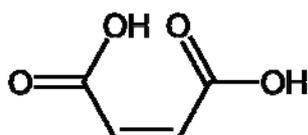
## 1. INTRODUCTION

The application of chemically modified electrodes in electroanalysis offers several advantages. They can lower the overpotential, increase the reaction rate and sensitivity, and improve the selectivity [1–4]. Dopamine (DA) is an important neurotransmitter compound widely distributed in the brain for message transfer in the mammalian central nervous system. Low levels of DA are related to neurological disorders, such as schizophrenia, Parkinson's disease and to HIV infection [5,6]. Therefore, determination of DA has attracted much attention of researchers. Similarly, Uric acid (UA), (2,6,8-trihydroxypurine), is the final product of purine metabolism in the human body [7]. In general, electroactive UA can be irreversibly oxidized in aqueous solution and the major product is allantoin [8,9]. It is one of the major parameters monitored in urine and in blood. Uric acid concentration changes are associated with the altered metabolism of purines that are related to numerous illnesses and physiological disorders [10]. Therefore, its determination in physiological fluids is necessary in the diagnosis and treatment of diseases such as gout, hyperuricemia, heavy hepatitis, and Lesch–Nyhan syndrome [11]. Uric acid is also a marker for renal failure as well as toxicity. Most analytical methods applied in routine clinical analysis, including uric acid assays, use an optical detection [12]. Therefore, the determination of UA with a simple method is essential because it serves as a marker for the detection of the above diseases. In voltammetric methods, the oxidation potentials of UA and DA, at the most usual electrode surface, are too close to be simultaneously determined. Therefore, it is important to develop simple, rapid and sensitive methods for their simultaneous determination in routine analysis. To achieve this purpose, various modified electrodes have been used for UA determination in the presence of DA [13-14].

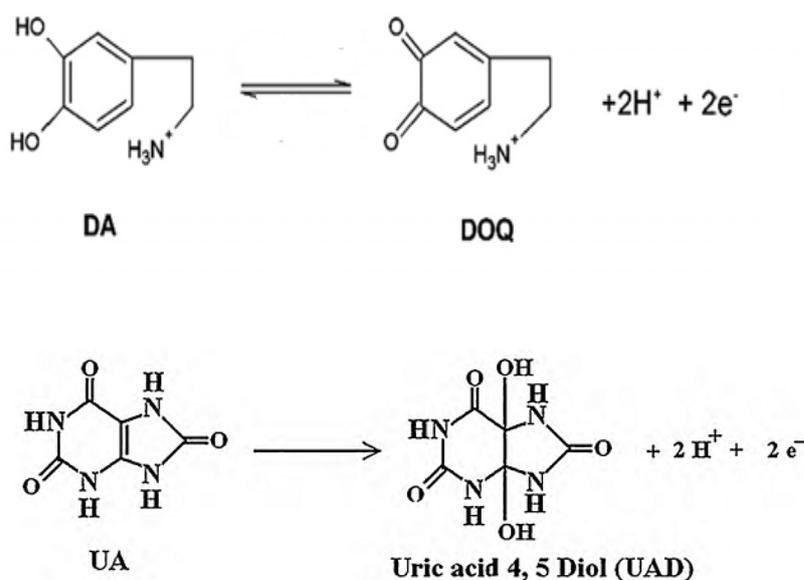
Polymer-modified electrodes prepared by electropolymerization have received extensive interest in the detection of analytes because of its high selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the films [15,16]. Protiva Rain Roy group [17] has reported Simultaneous electroanalysis of dopamine and ascorbic acid using poly-(N,N-dimethylaniline) modified electrode. Milczarek and Ciszewski reported an electrode modification with polymeric film of 2,2-bis(3-Amino-4-hydroxyphenyl) hexafluoropropane and electrocatalytic activities toward the oxidation of DA, UA and AA [18]. Recently related works have been done by our research group [19-24]. Scheme of oxidations of DA and UA is shown in scheme 2.

Maleic acid (Scheme.1) is widely distributed in small amounts in many natural food products. It is the predominant acid in many fruits, being known as “apple acid” because it is found in high concentration in apples, apricots, peaches, grapes as well as various citrus fruits, berries, Figs., carrots, peas, beans and tomatoes. And the selective methods based on existing biosensor technology to determine maleic acid all so reported [25].

The aim of our work was to fabricate stable electrode by electropolymerizing maleic acid on the surface of carbon paste electrode to achieve the challenge of simultaneous determination of DA in the presence of UA in physiological pH. Although no examination of the detection of dopamine in the presence of uric acid in physiological pH at poly (maleic acid) film coated carbon paste electrode has been reported. This novel work discussed about sensitivity, selectivity and reproducibility of neurotransmitter at poly (maleic acid) filmcoated carbon paste electrode at physiological pH.



**Scheme 1.** Structure of maleic acid



**Scheme 2.** Electrochemical oxidation of dopamine and Uric acid

## 2. EXPERIMENTAL

### 2.1. Apparatus and reagents

Cyclic voltammetric experiments were carried out with a model CHI (Model 680) connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare or poly(maleic acid)

modified CPE was used as a working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. All potentials reported were versus the SCE.

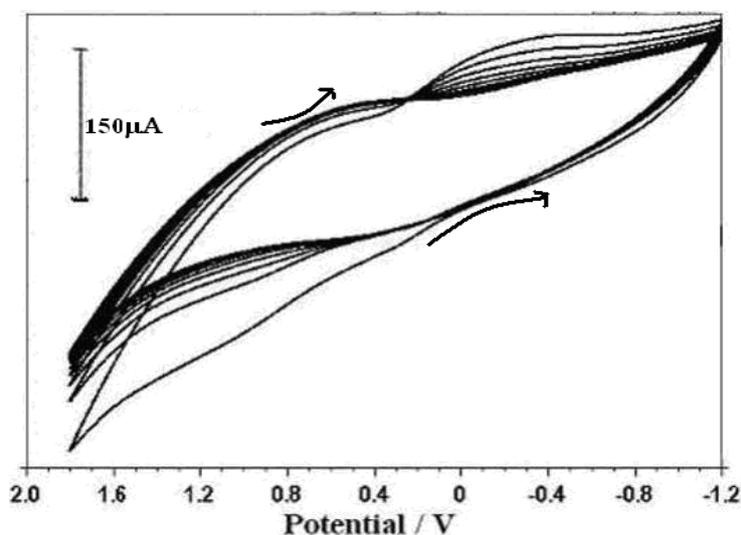
Dopamine hydrochloride (DA), Maleic acid and Uric acid (UA) were obtained from Himedia chemicals and were used as received. All other chemicals were of analytical grades. 0.2 M phosphate buffer solutions were prepared by mixing standard stock solutions of 0.2 M  $\text{Na}_2\text{HPO}_4$  and 0.2 M  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . Freshly prepared solutions of DA and UA were used in all experiments. All other the solutions were prepared with double distilled water.

## 2.2. Preparation of bare carbon paste electrode

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

## 2.3. Preparation of pre treated and poly (maleic acid) modified CPE:

The pretreated modified carbon paste electrode was prepared by scanning the bare CPE in the potential range from -400 to 1200 mV in 0.05 M  $\text{H}_2\text{SO}_4$  containing 1 mM maleic acid at  $100 \text{ mVs}^{-1}$  for 10 times. After this, electropolymerisation was enforced under sweeping from -400 to 1200 mV at  $100 \text{ mVs}^{-1}$  for 10 cycles in 0.01 M NaOH containing 1 mM maleic acid as shown in Fig.1 after polymerization the poly(maleic acid) modified CPE was rinsed with water and used for the determination of DA and UA.

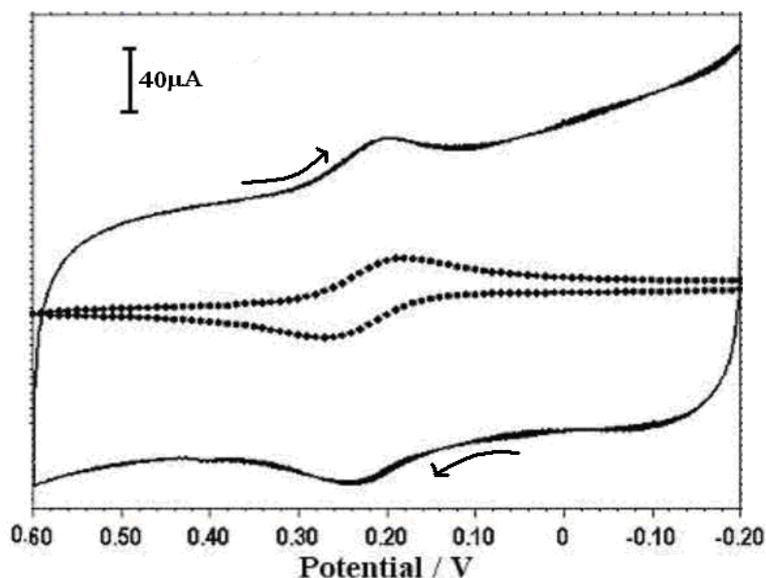


**Fig. 1.** Cyclic voltammogram of preparation of poly (maleic acid) film coated CPE. In 0.01 M NaOH, 1 mM maleic acid for 10 cycles at sweep rate of  $0.1 \text{ Vs}^{-1}$

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Electrochemical investigation of potassium ferrocyanide at poly(maleic acid) modified CPE

The characterization of poly(maleic acid) modified carbon paste electrode was investigated with standard  $[K_4Fe(CN)_6]$  by using CV technique. Fig. 2 shows the typical cyclic-voltammogram for 1 mM  $[K_4Fe(CN)_6]$  at both BCPE and poly(maleic acid) modified carbon paste electrode. The electrochemical reaction was carried out using 1 M KCl as supporting electrolyte.



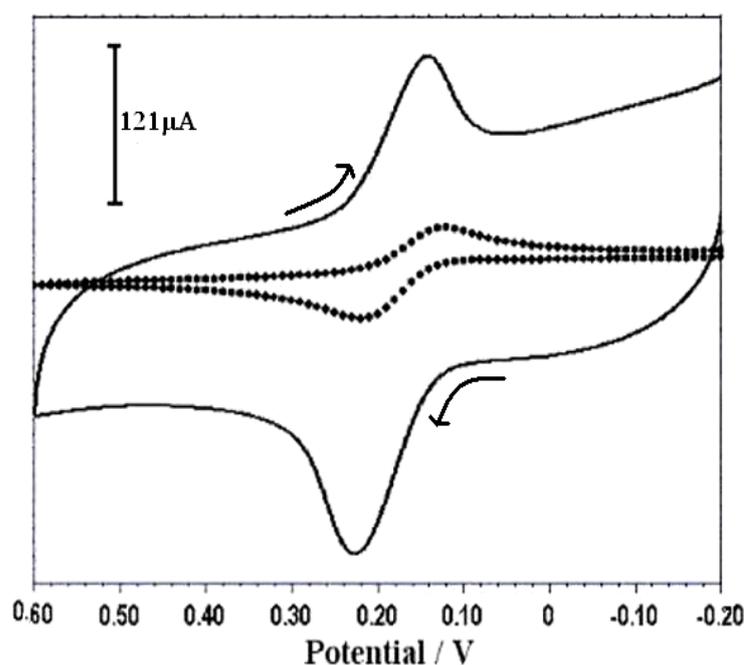
**Fig. 2.** Cyclic voltammograms for the electrochemical responses of  $K_4[Fe(CN)_6]$  at bare (dotted line) and poly (maleic acid) modified CPE (solid line) in 1 M KCl containing 1 mM  $K_4[Fe(CN)_6]$  at scan rate  $0.1 \text{ Vs}^{-1}$

Quasi-reversible voltammogram was observed for  $[K_4Fe(CN)_6]$  at BCPE(dotted line) with small cathodic peak current ( $I_{pc}$ ) and anodic peak current ( $I_{pa}$ )(dashed line). The cathodic peak potential and ( $E_{pc}$ ) and anodic peak potential ( $E_{pa}$ ) were located at 0.181 V and 0.270 V respectively. The potential difference of two reversible peaks was found to be 0.89 V. On modification with poly(maleic acid) the voltammogram has shown enhancement in both  $I_{pc}$  and  $I_{pa}$  (solid line). The  $E_{pa}$  and  $E_{pc}$  were found at 0.245 V and 0.193 V and potential difference was 0.052.

#### 3.2. Electrochemical investigation of dopamine at the poly(maleic acid) modified CPE

Fig. 3 shows at the surface of the modified electrode, the direct oxidation of DA produces a pair of redox peaks. The oxidation and reduction peak potentials occurred at 0.219 and 0.123 V, respectively. Under the identical conditions, the poly(maleic acid) modified CPE

gives increased peak currents to DA. A well defined redox wave of DA was observed with the anodic peak potential at 0.226 V and the corresponding cathodic peak potential at 0.140 V. So, the peak separation was smaller than that at the bare CPE, and further, substantial increases in peak current were also observed due to the improvements in the reversibility of the electron transfer processes. This suggests an efficient oxidation reaction of DA at the poly(maleic acid) modified CPE. By using poly(maleic acid) as an electron mediator in the matrix of the modified electrode, the over-potential for the anodic oxidation of dopamine becomes considerably lower and the rate of the heterogeneous electron transfer is increased.

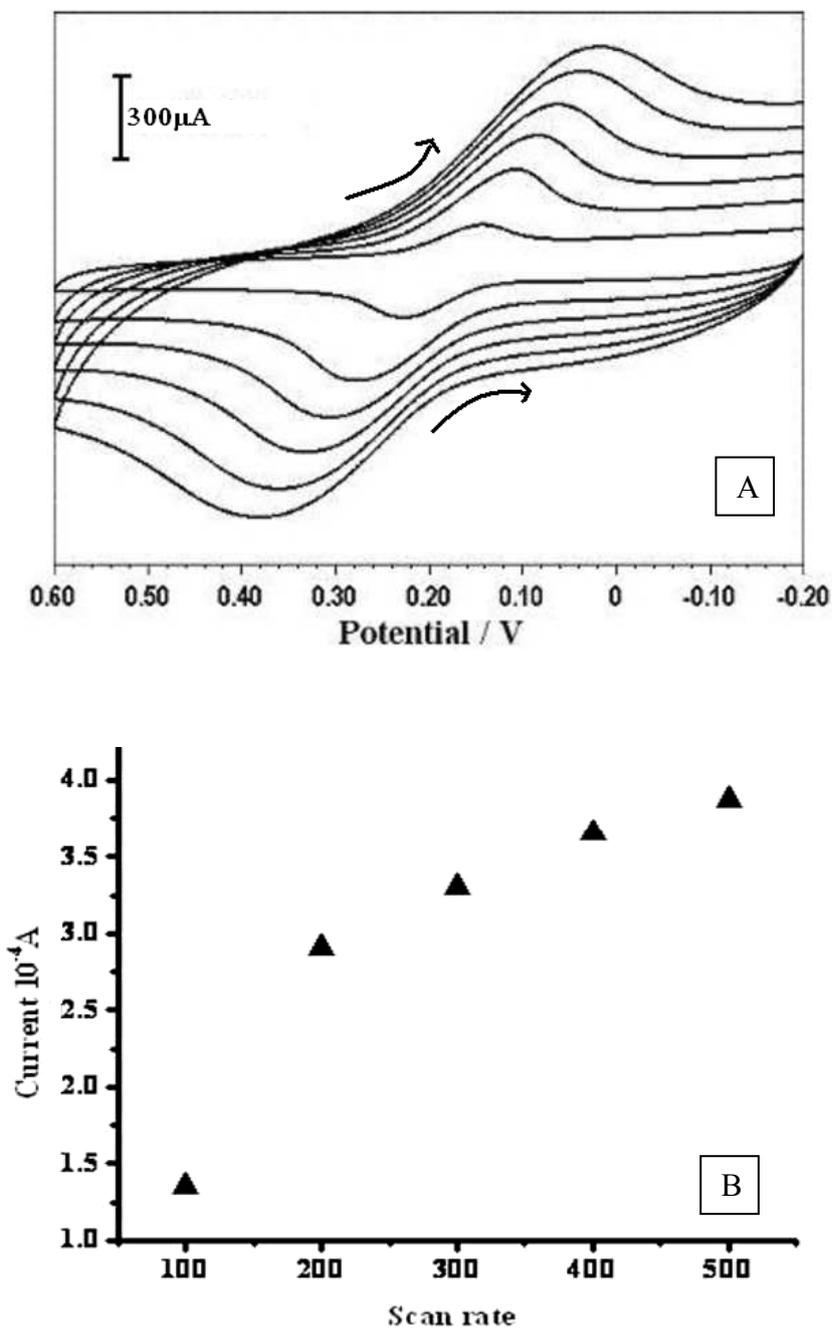


**Fig. 3.** Cyclic voltammogram of 1 mM DA in 0.2 M phosphate buffer solution of pH 7 at bare CPE (dotted line) and poly (maleic acid) film coated CPE (solid line)

### 3.3. Effect of scan rate on the peak currents of dopamine

Scan rate can influence the current responses of DA and corresponding electrochemical parameters could be deduced from the relationship between scan rate and current responses of DA. The dependence of oxidation peak current on 1 mM DA on scan rate at the poly(maleic acid) modified CPE in 0.2 M phosphate buffer (pH = 7), was illustrated in Fig. 4. As the scan rate increased the oxidation peak current ( $I_{pa}$ ) increased. The  $I_{pa}$  was directly proportional to the scan rate, ( $\nu$ ) over the range of 100–500  $\text{mVs}^{-1}$ . This result indicates that the overall electrochemical reaction of DA at the modified electrode might be controlled by the adsorption of DA as well as by a kinetic process. In addition, with increasing scan rate,

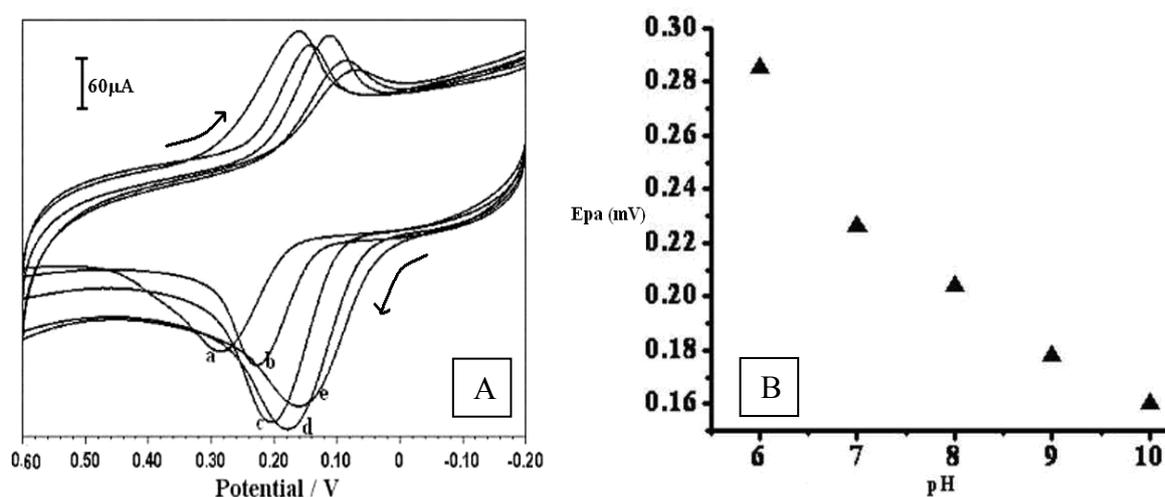
the catalytic oxidation peak potential ( $E_p$ ) shifts to more positive values and there correlation co-efficient =0.9141 as is illustrated in Fig.4.



**Fig. 4 (a).** Cyclic voltammograms of 1 mM DA on the poly (maleic acid) modified CPE at different scan rates (0.1, 0.2, 0.3, 0.4, 0.5  $\text{Vs}^{-1}$ ) in 0.2 M phosphate buffer solution pH 7.0; **(b).** The plot of the anodic peak current versus the scan rate

### 3.4. Effect of the solution pH

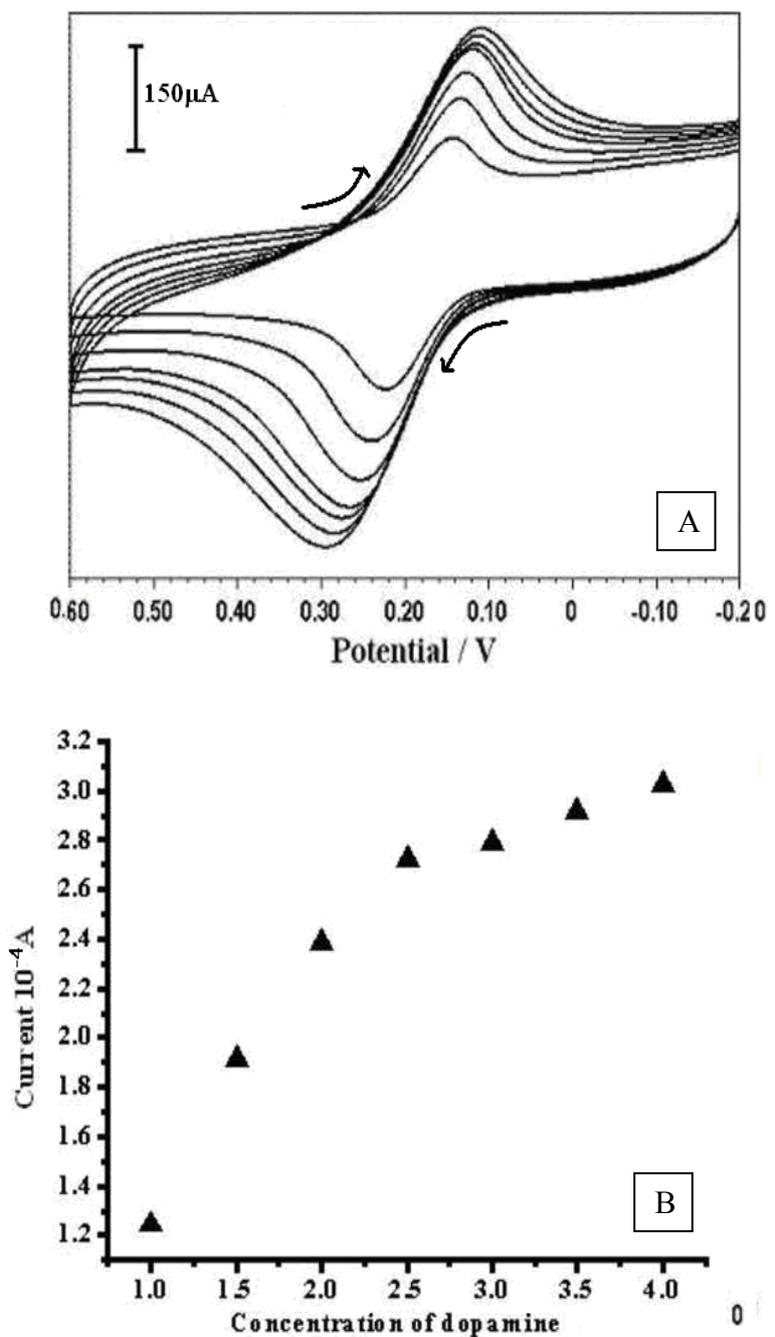
The effects of the pH on the electrode response and the oxidation potential were investigated by the cyclic voltammetric technique. As shown in Fig. 5 it can be seen that the anodic peak current of DA increased slightly with increasing pH until it reached about 9, and then decreased when the pH increased further. Furthermore, the  $E_{pa}$  vs. pH graph clearly shows that the catalytic peak shifts to a more negative potential with increasing the pH in the range of 6–10. The linear-regression equation was  $E_{pa}(\text{V})=0.5821-0.0497 \text{ pH}$ , with a correlation coefficient of 0.96995 (Fig. 5b) with a slope of 29 mV/pH which indicated that the proportion of electrons and protons involved in the redox of DA was 1:1 [26].



**Fig. 5 (a).** Cyclic voltammograms obtained at the poly (maleic acid) modified CPE in 0.2 M phosphate buffer solutions in pH values, (a) 6 (b) 7 (c) 8 (d) 9(e) 10 containing 1 mM DA at scan rate of  $100 \text{ mVs}^{-1}$ ; **(b).** The plot of standard redox peak potential ( $E_{pa}$ ) of DA on cyclic voltammograms versus pH values

### 3.5. Effect of concentration of DA

The effect of the DA concentration on the voltammetric response of the poly(maleic acid) modified electrode was investigated. The cyclic voltammograms were obtained in a series of concentration of DA (Fig. 6). Upon the addition of DA, there was a dramatic enhancement in the anodic current. The dependence of peak current on the concentration of DA was a linear relationship in the range from 1 to 4 mM with the correlation coefficient,  $r=0.93013$  (Fig. 6b).

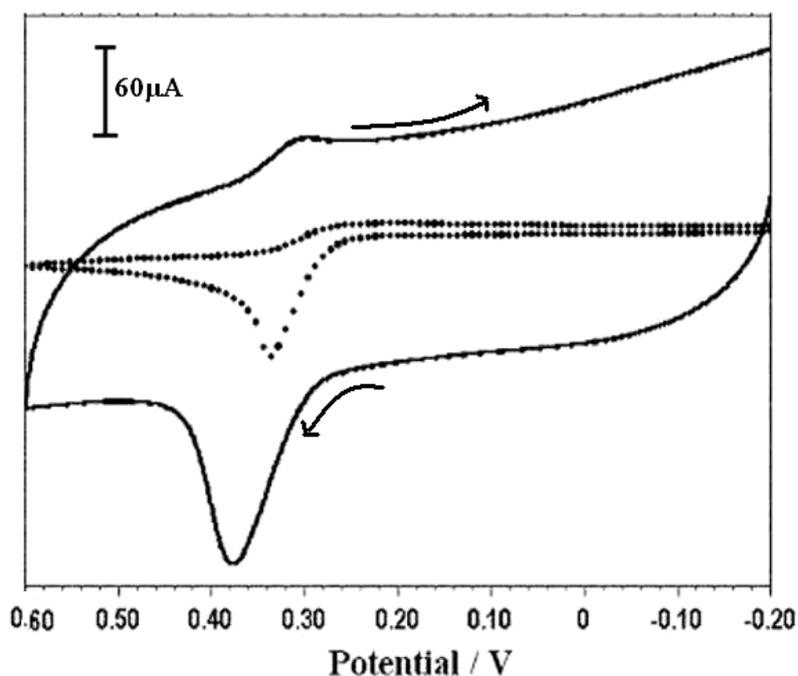


**Fig. 6 (a).** Cyclic voltammogram of DA at different concentration (1-4 mM ); **(b).** Graph of current vs. concentration of DA

### 3.6. Electrochemical response of Uric acid at the poly(maleic acid) modified CP

Fig. 7 illustrates the Cyclic voltammogram of UA at the bare and poly(maleic acid)-modified carbon paste electrodes in phosphate buffer (pH 7). At the bare electrode, the CV exhibited a broad peak at a higher potential about 0.337 V with poor current response for UA oxidation. In contrast, at the poly(maleic acid)-modified electrode, a positive shift of the

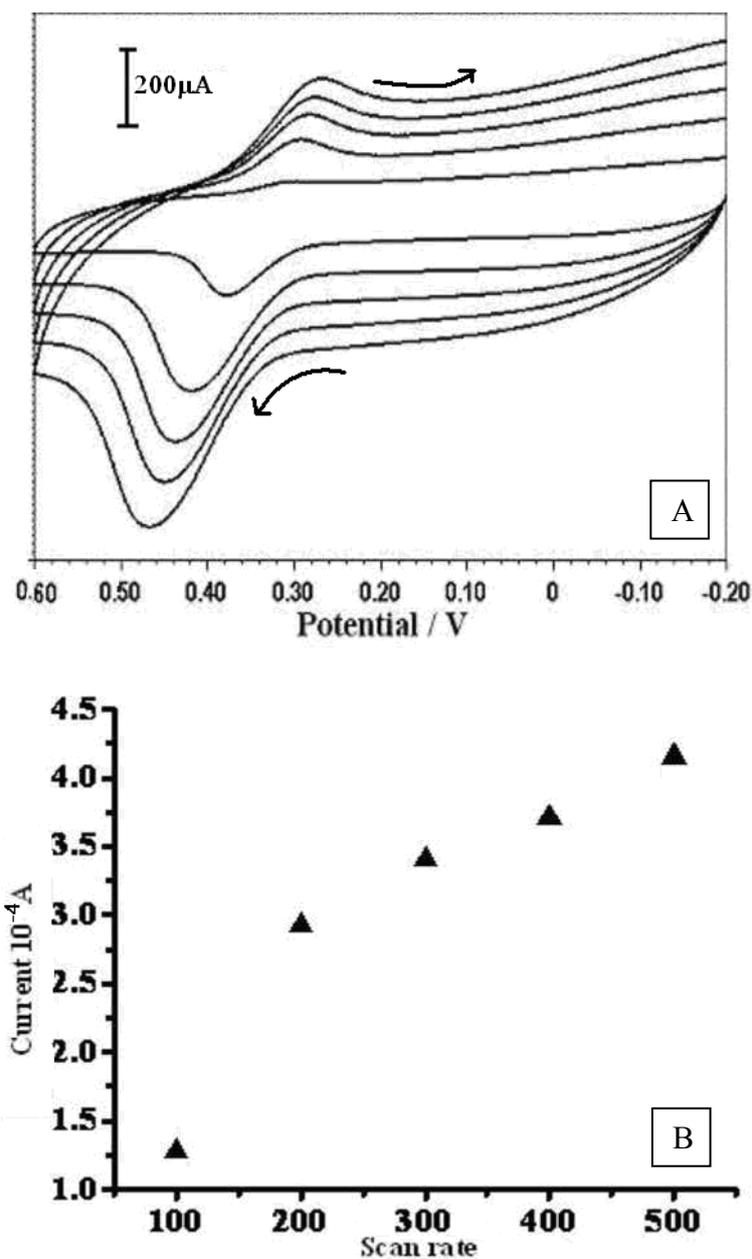
oxidation potential to 0.378 V and an increase in peak current were observed, which indicated that the poly(maleic acid)-modified electrode possessed a strong electrocatalytic activity for the oxidation of UA.



**Fig. 7.** Cyclic voltammograms obtained for the oxidation of 1 mM UA at poly (maleic acid) MCPE (solid line) and BCPE (dotted line) at scan rate  $0.1 \text{ Vs}^{-1}$

### 3.7. Effect of scan rate on the oxidation of UA

Fig. 8 shows the CV of the poly(maleic acid) modified carbon paste electrode at various scan rates obtained in phosphate buffer (pH 7) containing 1 mM of UA. The peak current was proportional to the scan rate in the range of  $100\text{--}500 \text{ mVs}^{-1}$  with a correlation coefficient of 0.9301 (Fig. 8b) for the anodic oxidation of UA, indicating that the catalytic reactions were controlled by adsorption.

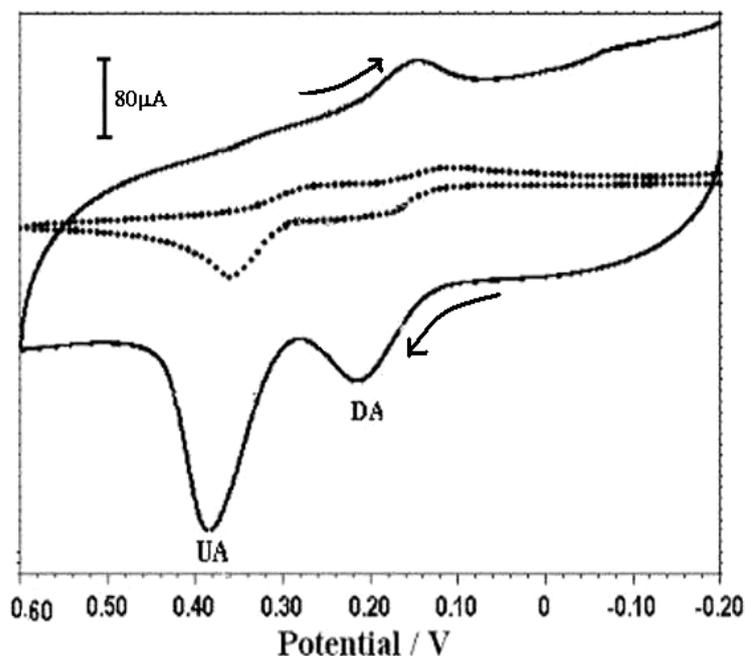


**Fig. 8(a).** Cyclic voltammograms for the oxidation of 1 mM UA at different scan rate 0.1-0.5  $\text{Vs}^{-1}$  in 0.2 M phosphate buffer solution (pH 7.0); **(b).** The plot of anodic peak current versus scan rate

### 3.8. Simultaneous determination of DA and UA at poly(maleic acid) modified carbon paste electrode

To evaluate the sensitivity and selectivity of the present system for the quantification of UA and DA, the electrochemical behavior of mixture of UA and DA at the poly(maleic acid)-modified electrode was studied. The results showed that at the bare carbon paste electrode, the CV of phosphate buffer (pH 7) had no reduction peak and that of the mixture of UA and DA in phosphate buffer had only an oxidation peak at 0.217 V (Fig. 9) illustrating that the

oxidation peaks of UA and DA could not be well separated at the bare electrode. In contrast, two well-defined anodic peaks at the potentials of 0.384 and 0.216 V and one reduction peak potential of 0.145 V were observed for the oxidation of UA (1 mM) and DA (0.5 mM), respectively, at the modified electrode. The observed CV changes indicated that the modified electrode had a good catalytic activity for the oxidation of UA and DA and could clearly distinguish UA and DA.



**Fig. 9.** Simultaneous determination of 0.5 mM DA, and 1 mM UA at bare CPE (dotted line) and at poly(maleic acid)film coated CPE (solid line)

#### 4. CONCLUSION

The poly(maleic acid) film was prepared and used as a modified electrode in a neutral solution for the determination of UA and DA, and their mixture by Cyclic voltammetric technique. A clear separation of oxidation peaks of UA and DA could be achieved, indicating that the poly(maleic acid) electrode facilitated the simultaneous determination of UA and DA with good stability, sensitivity, selectivity, with satisfactory results.

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