

Full Paper

PhosphoMolybdic Acid and Poly(Paraphenylenediamine) Modified Carbon Paste Electrode using Voltammetric Determination of Dopamine and Uric Acid

Gundluru Bhagya Lakshmi,¹ Yellala V. Rami Reddy,^{1,*} and Raminani Ravi²

¹*Department of Chemistry, S V University, Tirupathi, A. P., India*

²*Department of Chemistry, Govt Degree College, Pakala, Chittoor Dist, A.P., India*

*Corresponding Author, Tel.: +919440450108

E-Mail: dryvrsvu@gmail.com

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Abstract- A polymerized film of PhosphoMolybdic Acid (PMA)/Poly(Paraphenylenediamine) (PPD) was prepared. The surface of carbon paste electrode was polymerized with the film of PhosphoMolybdic Acid (PMA) and paraphenylenediamine in PBS buffer solution of physiological pH 7.4 by the process of ionic deposition and electro-polymerization. Electrochemical identifications were studied by cyclic voltammetry. This Modified Carbon Paste Electrode (MCPE) was used to investigate DP and UA by CV and DPV techniques, number of parameters affecting the electrocatalytic activity of modified CPE such as effect of pH, scan rate, and concentration were studied. The detection limits of dopamine (DP) and Uric Acid(UA) were calculated by CV as 1.3550 μ M and 4.230 μ M respectively. The high electro catalytic activity of PMA and PPD modified carbon paste electrodes expected to be highly applicable in the field of electro analytical chemistry for the determination of other bio active molecules or neurotransmitters. The modified electrode showed higher sensitivity and selectivity for the simultaneous determination of DP and UA, and fouling effect is also eliminated by this MCPE.

Keywords- Dopamine; Uric acid; Phosphomolybdic Acid; Paraphenylenediamine; Carbon paste electrode

1. INTRODUCTION

Electroanalysis involves the most exiting research area as the simultaneous and interference free investigation of bioactive functional groups [1-3]. Electroanalytical procedures have their widespread because of many users such as fast, dependable response, reproducible cost, and smooth working methods [4-7]. Electroanalytical scientists kept their attention to resolve electroactive molecules by CV from past decades, and modifications at carbon paste electrode shows excellent properties to the CV determinations. By applying simple molecules through electro polymerization on CPE gives good results and literature clearly explained the modifications on CPE [8-13].

Uri acid (UA) is the important bioactive molecule that's present in the human body which includes urine and blood. The principal main product of purine metabolism is the Uric acid. When the uric acid levels turns into changed in blood and urine may object some diseases particularly Hyperuricemia, gout and the Lesch-Nyan disease. Normally in human blood, serum levels contain UA range from 41 to 88 mg/ml and also urinary excretion is 250 -750 mg per day [14-17]. In the field of drug discovery and analysis the diseases, the researchers mainly focuses on to developing the various electrochemical sensors for the UA [18].

Dopamine (DP), which is also predictable as "4-(2-aminoethyl) benzene-1, 2-diol" belongs to the member of catecholamine family. Mammalian brain tissues and fluids mainly contains DP, which is most important neurotransmitter and it exhibits its activity on central nervous system [CNS]. Number of diseases such as Parkinson, Alzheimer's are caused due to the dopaminergic neurons malfunctions [19]. In addition, dopamine is broadly used in the treatment of diseases caused by myocardial infarction [circulatory collapse syndrome], trauma renal failure, and cardiac surgery [20]. In the brain, dopamine capabilities as a neurotransmitter activating dopamine receptors and is produced in a variety of regions of the brain which consist of the massive nigra and the ventral segmental area [21-24].

Phosphomolybdic acid (PMA), also referred to as dodecamolybdophosphoric acid, which is a yellow solid and likely soluble in water and ethanol. PMA is widely used in organic synthesis and as a spatter in the study of microscopic structure of tissues [25]. Phosphomolybdic acid is also acts as catalyst in Skraup reaction which is the synthesis reaction for quinolines [26]. *p*-Phenylenediamine (PPD) is an ordinary compound with the molecular formula $C_6H_4(NH_2)_2$, which is a derived from aniline which is a white solid, conversely samples can darken because of air oxidation [27]. PPD specially utilized as element of polymers preparation and composites like Kevlar. The utility of electrochemical strategies to the determination of hair dye constituents became investigated [28]. In this established work PPD was used as modifier for the fabrication of PMA and PPD changed carbon past electrode (CPE), for the cyclic voltammetric (CV) and differential pulse voltammetric (DPV) determinations of DP and UA. Very good electrocatalytic activity and well separated signals

for DP and UA were obtained by this fabricated electrode with high sensitivity at generalized pH.

2. EXPERIMENTAL

2.1. Instrumentation and Reagents

PDD, UA, DA, PMA have been obtained from Himedia, PMA and PPD twisted into made with double distilled water. To obtain results preferred PH, PBS is used by proper combining of suitable amounts 0.2M NaH_2PO_4 and 0.2M Na_2HPO_4 . Analytical grade quality chemicals were used. The electrochemical investigations have been carried out by a potentiostate model CHI-660c (CH Instrument-660 electrochemical workstation), which contains three electrode setup with PMA and PPD modified carbon paste as a working electrode, platinum wire as an auxiliary electrode, and saturated calomel electrode as reference electrode. At room temperature $25 \pm 0.5^\circ\text{C}$ all experiments were presented.

2.2. Preparation of BCPE

In the development of a bare carbon paste electrode (BCPE), homogenous paste of carbon was produced by proper combining of 70% graphite and 30% silicon oil in an agate mortar, then the formed carbon pastes was introduced within a cavity of Teflon tube and soften on a weighing paper. Now the electrode was provided with an electrical contact by copper wire which was connected to the paste at the end of the tube. By using this electrode, the obtained voltammogram of analytes are shown in the following Fig. 1.

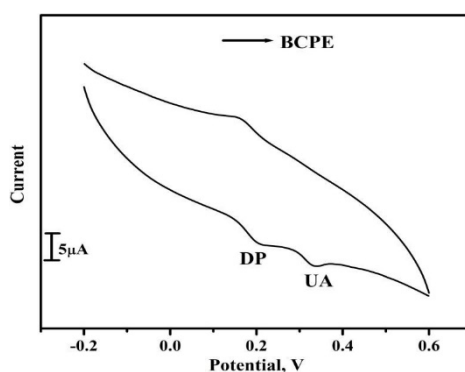


Fig. 1. A cyclic voltammogram bare carbon paste electrode of 0.2M PBS at pH7.5

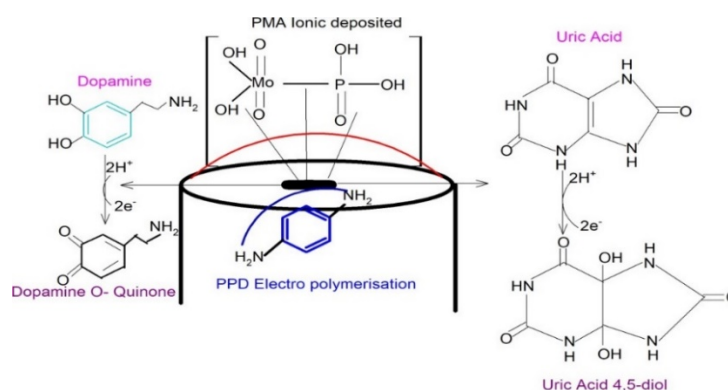
3. RESULTS AND DISCUSSION

3.1. Electrochemical ionic deposition of PMA and electro-polymerization of Paraphenylenediamine on the surface of CPE and its characterization

The polymer modified carbon paste electrode was fabricated by electrochemical ionic deposition of PMA and polymerization of 0.1mM PPD by cyclic voltammetry in 0.2M PBS at

physiological pH 7.4 within potential range from -0.6V to +1.6V and applied scan rate is 0.1Vs^{-1} . The distortion is observed within potential range less than -0.6V [30-32]. If the polymer thickness of the film increased it stops the process of transferring of electrons within the 0.1Vs^{-1} scan rate. A rise in redox current in cyclic voltammogram was seen in Fig. 2, and Fig. 3.

Which is preliminary indication of 0.21V DP and 0.33V UA also reflected in development of electro active layer on surface of CPE. Rise in the redox peak current was constant and steadier after some tentative sweeps indicating the degree of saturation in electro active polymer growth [12,31-32]. When the sweep segments are increased the fabricated electrode exhibits good electrocatalytic response, but when there were more than fifteen polymerizing cycles the peak currents in the determination of DP and UA began steadier. In addition the higher the density (heaviness) of the polymeric film, the working electrode corresponding electro catalytic activity disappears. Therefore in fabricating a stable PPD MCPE for the determination fifteen cycles was taken as best. The possible electro ionic deposition of PMA and the electro polymerization of PPD on the CPE surface are shown in Scheme 1.



Scheme 1. The electro ionic deposition and electro chemical polymerization of the carbon paste electrode surface and Dopamine ad Uric Acid oxidation reaction in electrochemical cell

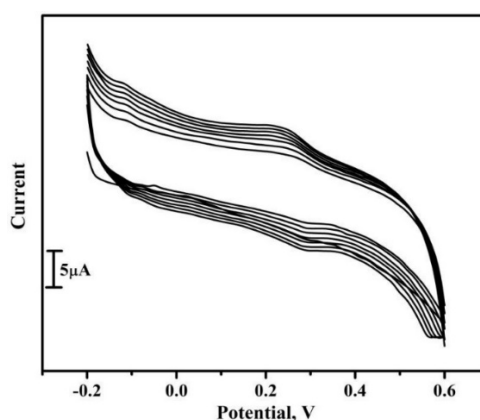


Fig. 2. Cyclic voltammograms obtained for the electro ionic deposition of 1.0 mM PMA, and electro polymerization of 1.0mM PPD on CPE surface in 0.2M PBS of pH 7.5 at scan rate of 0.1Vs^{-1} for 15 cycles

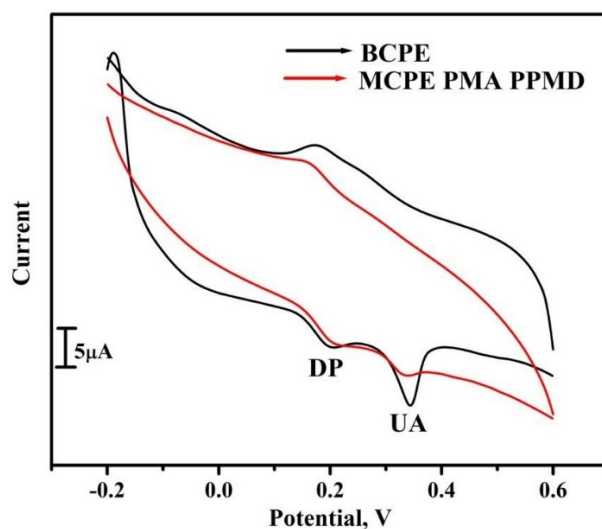


Fig. 3. Cyclic voltammograms for simultaneous determination of binary mixture of (0.1mM) DP and UA at BCPE and PMA and PPD MCPE with 0.05Vs^{-1} scan rate

3.2. Influence of scan rate on the oxidation of DP and UA

The study of potential scan rate on the electrode process explains electrode kinetics among the solute-solvent interfaces. Implemented scan rates for the binary mixture (0.1mM) of DP and UA oxidation in 0.2M PBS of pH 7.5 cyclic voltammetric approach at PMA and poly(paraphenylenediamine) MCPE are stated in Fig. 4. From Randles-sevick's equation the scan rate is directly proportional to scan rate. The plot of anodic peak current (I_{pa}) versus scan rate (v) and (I_{pa}) versus square root of scan rate ($v^{1/2}$) was plotted for DP and UA and shown in Fig. 5 and 6; and Fig. 7 and 8; respectively.

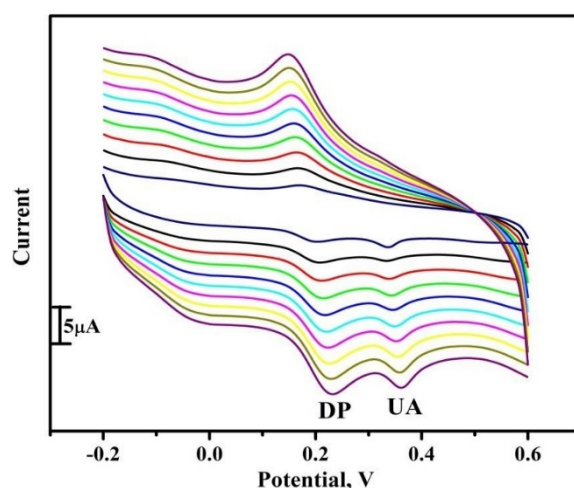


Fig. 4. Cyclic voltammograms of different scan rates ($0.05\text{-}0.5\text{Vs}^{-1}$) in 0.1mM DP and UA at 0.2M PBS of pH 7.4 at PMA and poly(paraphenylenediamine) MCPE

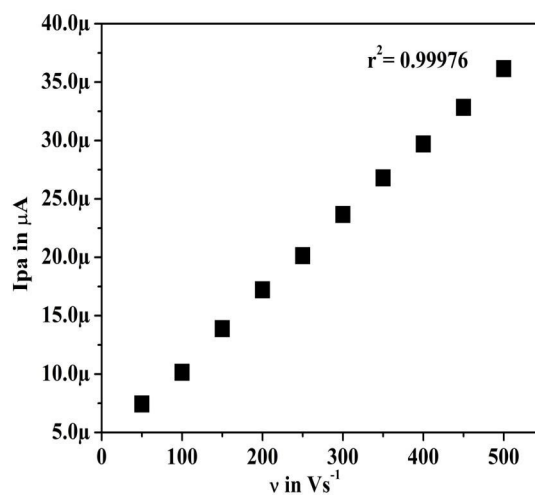


Fig. 5. Plot of I_{pa} vs. UA scan rate

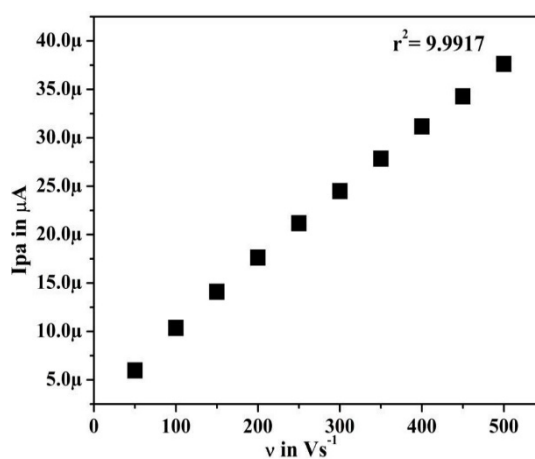


Fig. 6. Plot of I_{pa} versus DP scan rate

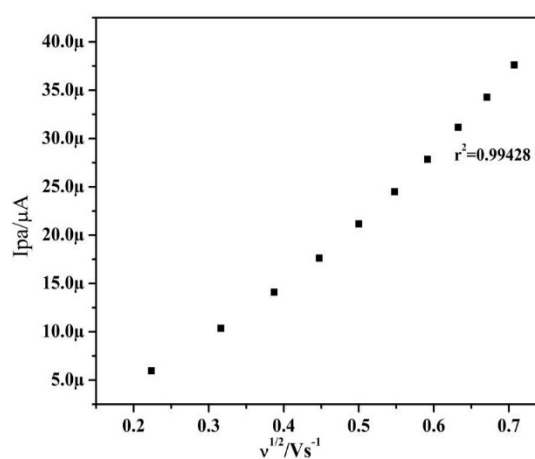


Fig. 7. Plot of I_{pa} vs. $\nu^{1/2}$ DP

The graphs acquired were almost straight lines. Anodic peak currents were linearly proportional to the scan rate and square root of scan rates and their correlation coefficients for I_{pa} vs. v and $v^{1/2}$ is $r^2=0.992$, $r^2=0.994$ for DP and I_{pa} vs. v and $v^{1/2}$ is $r^2=0.999$, $r^2=0.990$ for UA within the range of $0.02-0.2 \text{ Vs}^{-1}$. this information about anodic peak current versus scan rate concludes that electron transfer reaction is a diffusion-controlled method at the MCPE surface [34-36].

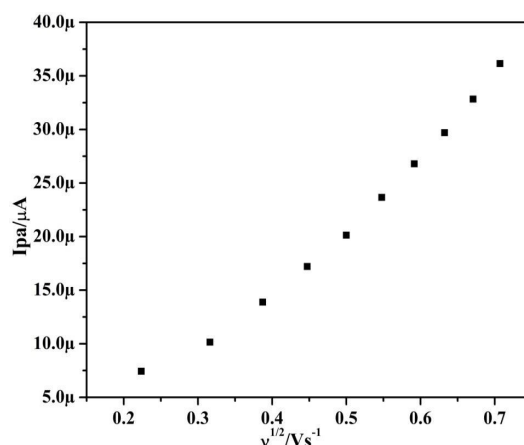


Fig. 8. Plot of I_{pa} vs. $v^{1/2}$ UA

The DP and UA oxidations for PMA and poly(paraphenylenediamine) MCPE were calculated from the various experimental scan rate values are revealed in Table 1.

Table 1. The experimental different Scan rate values

$v \text{ (Vs}^{-1}\text{)}$	$\Delta I_{pa} \text{ (V)}$	
	Dopamine (DP)	Uric Acid (UA)
50	5.971	7.433
100	1.0359	1.015
150	1.4097	1.388
200	1.7626	1.720
250	2.117	2.013
300	2.4498	2.366
350	2.784	2.679
400	3.1162	2.969
450	3.4273	3.283
500	3.7616	3.615

3.3. Effect of DP and UA concentration

Cyclic voltammograms of DP and UA with different concentrations (1 to 4 μM) were obtained by PMA and poly(paraphenylenediamine) MCPE at 0.2M PBS of pH 7.5 at the scan rate of 0.1Vs^{-1} , and this is explained in Fig. 9, 9B and Fig.10. Then, Fig. 9 and Fig. 10, show that with increased concentration, the peak current of DP and UA raised, which concludes linear relationship between anodic peak current and concentration. The graph of I_{pa} versus concentration explains linear relationship and equation of linear regression is $I_{\text{pa}} (\mu\text{A}) = 0.607(C^0 \mu\text{M/L}) + 1.635$, ($r^2=0.999$) and $I_{\text{pa}} (\mu\text{A}) = 0.6957(C^0 \mu\text{M/L}) + 1.5409$, ($r^2=0.962$) for DP and UA respectively.

The study of LOD and LOQ was deliberated by following equations. Where S is the standard deviation of mean value, the working curve slope is M [32,38].

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

$$\text{LOQ} = 10 S/M \quad (4)$$

Observed values of LOD and LOQ for both DP and UA were represented in Table 2 along with PMA and poly(paraphenylenediamine) MCPE. And also Table 2 explains the lower limits of detection of DP and UA for PMA and poly PPD MCPE than other modified carbon paste electrodes [31-32,34,39,40].

Table 2. Comparative study of the LOD's of DP and UA with various modified electrodes along with PMA and poly(paraphenylenediamine) MCPE

Working electrode	Limit of Detection In μM		Method	References
	Dopamine (DP)	Uric Acid (UA)		
Pdop@GR/MWCNTs	-	15.0	CV	[41]
Mp-GR	-	2.0	CV	[42]
FCNSPE	-	0.042	CV	[43]
DNA/PAMAM/MWNT-Chit/Au	-	0.07	CV	[44]
MIP-Si-ITOA/electrode	2×10^{-6}	-	CV	[45]
GSCRF-MIPs/GCE	1.46×10^{-7}	3.5	CV	[46]
Imprinted PPy/GCE	5.7×10^{-12}	-	CV	[47]
PMA/poly (Paraphenylenediamine) MCPE	1.355×10^{-6}	4.230	CV	This Work

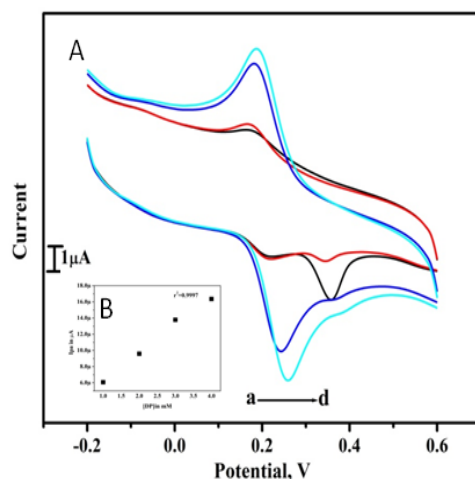


Fig. 9. A) Cyclic voltammograms of DP in 0.2M PBS solution of pH 7.5 at PMA and poly (Paraphenylenediamine) MGCE at scan rate of 0.05Vs^{-1} with different concentration (a–d; 1 to $4\mu\text{M}$) B) Graph of anodic peak current versus concentration of DP

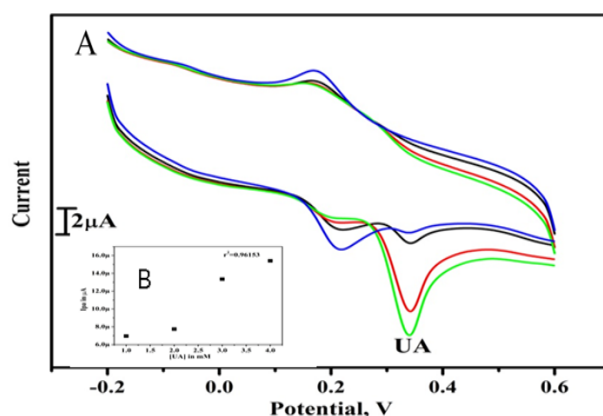


Fig. 10. A) Cyclic voltammograms of UA in 0.2M PBS solution of pH 7.5 at PMA and poly (paraphenylenediamine) MGCE at scan rate of 0.05Vs^{-1} with different concentration (a–d; 1 to $4\mu\text{M}$); B) Graph of anodic peak current versus concentration of UA

3.4. Influence of pH on DP and UA oxidation

In the electrochemical determination of molecules that are electro active, pH of the Supporting electrolyte plays an important role. As shown in the Fig. 11A, Fig. 11B, Fig. 12A, Fig. 12B the effect of pH value on the cyclic voltammetric response of binary mixture containing $40\mu\text{M}$ DP and $40\mu\text{M}$ UA was investigate at PMA and poly (paraphenylenediamine) MCPE. 0.2M PBS was used to obtain cyclic voltammograms of DP and UA with different pH values and we can observe anodic peak potentials of DP and UA was moved to the more negative side as the pH of the solution increases. A linear relationship was formed between the

DP and UA anodic peak potentials (E_{pa}) versus the pH (PBS) in the range of 5.5 to 8.0. The equations of linear regression are $E_{pa}(V)=0.08-0.04$ (pH) ($r^2=0.996$) and $E_{pa}(V)=0.24-0.36$ (pH) ($r^2=0.965$) for DP and UA individually. The 1.24 and 1.25 slope for DP and UA oxidation indicates that similar number of electrons and protons are involved in the redox process which is stated by Nernst equation [11,31].

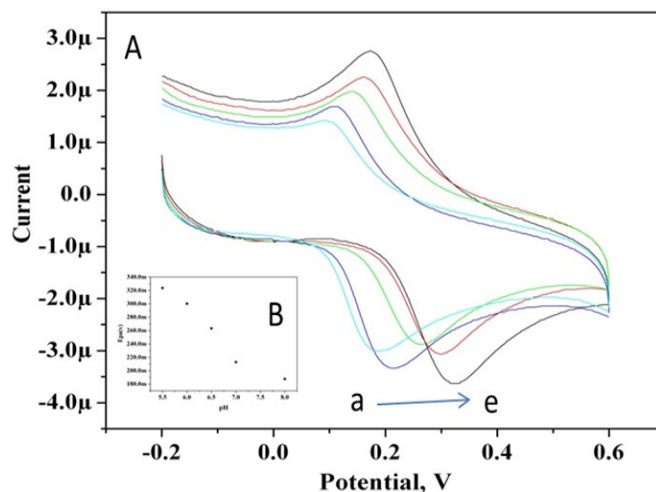


Fig. 11. A) Cyclic voltammograms of 0.1mM DA at various pH solutions (5.5 to 8.0) with the scan rate of 0.05Vs⁻¹; **B)** Graph of E_{pa} vs. pH

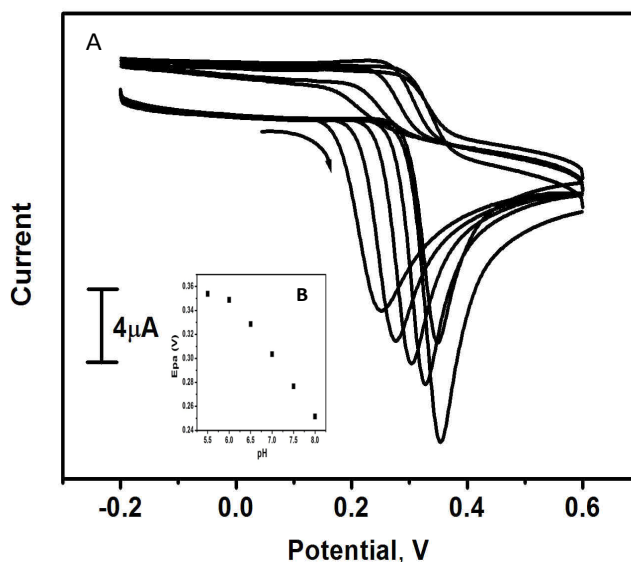


Fig. 12. A) A cyclic voltammograms of 50μA UA at PMA and poly(Paraphenylenediamine) MCPE in 0.2M PBS solution at different pH; **B)** A graph of the anodic peak potential of UA at PMA and poly (Paraphenylenediamine) MCPE at pH 5.5 to 8

3.5. Interference study

PMA and poly(paraphenylenediamine) MCPE was used to simultaneous determination of DP and UA, by differential pulse voltammetry (DPV) because of its more current sensitivity and lack of background current. Fig. 13 explains the DPV record of simultaneous analysis of 0.1mM DP and 0.1mM UA in 0.2M PBS of pH 7.4. And this determination was carried out when the concentration of one analyte was changed and the other remains constant. Fig. 14A and Fig. 14B explain that with increased concentration, the peak current of DP was raised and this concentration increased from 10.0 μ M to 40.0 μ M and it also shows that there is no difference in the peak current of UA. The selective oxidation was observed for DP at 0.1606V and for UA 0.3061V respectively, with a peak to peak separation was 0.1455V. Ultimately the results explained that precise and interference free identification of DP and UA was done by PMA and poly(paraphenylenediamine) MCPE.

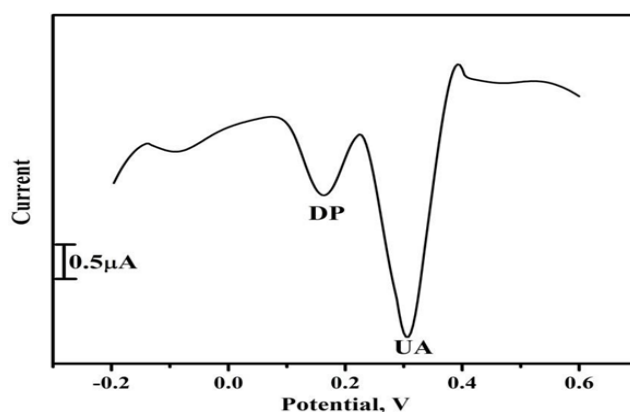


Fig. 13. DPVs obtained for 0.1mM DP and UA at PMA and poly(paraphenylenediamine) MCPE

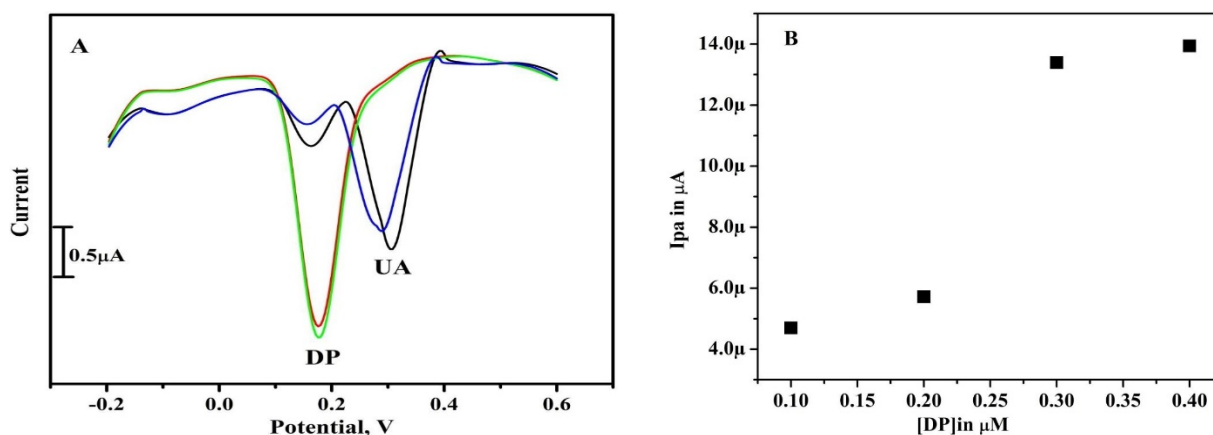


Fig. 14. A) DPVs of DP at various concentrations as (10.0 μ M-40.0 μ M) in 0.2M PBS of pH 7.4 in presence of 30.0 μ M UA at PMA and poly(paraphenylenediamine) MCPE; B) Plot of anodic peak current versus concentration of DP

4. CONCLUSION

The modified electrode was prepared by electro polymerization process and the electrochemical parameters are examined. The modified carbon paste electrode works effectively with regard to electrochemical exploration of DP and UA. The PMA/PPD modified electrode reveals low detection limits compared with previous literatures. The MCPE produces remarkable impact on redox peak currents for DP and UA with better electro chemical signal separation between DP and UA. The changed electrode has high electro catalytic activity with strong selectivity and sensitivity with regard to DP and UA concentration. The high electro catalytic activity of PMA and PPD modified carbon paste electrodes expected to be highly applicable in the field of electro analytical chemistry for the determination of other bio active molecules or neurotransmitters.

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