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# Sensitive Detection of Anthrone using Poly (L-Arginine) modified Carbon paste electrode by Voltammetric Method

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## ABSTRACT

*A sensitive method was developed for the detection of an Anthrone (ANT) using poly (L-Arginine) modified carbon paste electrode (MCPE). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used to investigate the electrochemical behavior of ANT in 0.2 M phosphate buffer solution (PBS) of pH 7.0 at poly (L-Arginine) MCPE. The poly (L-Arginine) MCPE shows a good electro catalytic activity towards the electrochemical behavior of ANT. A technique like Field emission scanning electron microscopy (FESEM) has been used to study the surface morphology of BCPE and MCPE. Detection of small amounts of ANT was done by using CV as an electrochemical sensitive analytical method. An effective linear range of $6\times10^{-6}$ to $1.0\times10^{-4}$ M with limit of detection $4.7 \times 10^{-6}$ M and limit of quantification $1.5 \times 10^{-5}$ M was obtained for ANT. The poly (L-Arginine) MCPE exhibited an excellent reproducibility, long-term stability, high sensitivity. These results offer the development of a simple, rapid response, and low cost electrochemical sensor and developed poly (L-Arginine) MCPE as an electrochemical sensor was successfully applied to detect the ANT by Cyclic voltammetric technique.*

**Keywords:** *Carbon paste electrode, L-Arginine, Anthrone, Cyclic voltammetry, Differential pulse Voltammetry*

## INTRODUCTION

ANT generally utilized in the colorimetric analysis of carbohydrates, and considered as a purgative in pharmacy and it is an aromatic ketone [1]. Long-term exposure to ANT leads to many aggravation, such as difficulty in breathing, and related problem such as respiratory irritation. In the last few years carbon based electrodes especially CPE and MCPE have also been integrated into the electrochemical sensor for the determination of biologically important compound due to their unique properties such as low background current, low cost, wide potential window, and renewability of the electrode surface. The aim of the polymeric compound film coated modified electrode sensor is one of the important tool for the analysis of biomolecules [2-3].

Electrochemical sensors and CPEs play a very crucial role in the fields like proteomics, molecular biology, pharmaceutical, environmental analysis [4-10].

Electrochemical techniques based on CPEs have a more draw of attention due to their high sensitivity, instrumental simplicity, moderate cost, easy portability, easy to prepare, good selectivity, and time saving for the determination of bioactive molecule [11-17]. Cyclic voltammetry [18-20] is one of the powerful electro analytical technique, which has been generally utilized to investigate the electrochemical behaviour of electro active species.

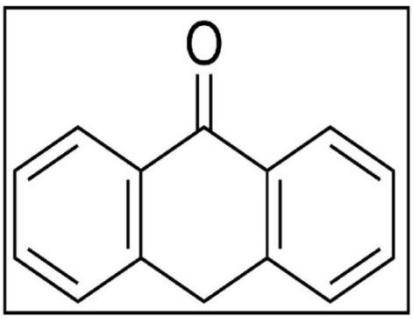

**Figure1.** *Structure of ANT*

A new electro analytical procedure was developed for the determination of ANT in this work. This present study aimed at the fabrication of poly (L-Arginine) MCPE towards the detection of ANT by CV technique that was investigated by the first time. The method offer low cost, simple, rapid response, and high

sensitivity for the detection of ANT. A well-resolved voltammetric response obtained for ANT at poly (L-Arginine) MCPE. Fig.1 shows the structure of ANT.

## Experimental Analysis

### Reagents and Chemicals

Graphite, silicone oil, and ANT were obtained from Nice Chemicals, India. Monosodium hydrogen phosphate, Disodium hydrogen phosphate, L-Arginine was purchased from Molychem, India. All chemicals were of analytical grade and used without any further purification. The stock solution of ANT ($25\times10^{-3}$ M) was prepared by using acetone. $25\times10^{-3}$ M L-arginine stock solution was prepared in distilled water. PBS (0.2 M) was prepared by mixing suitable amount of 0.2 M monosodium hydrogen phosphate and 0.2 M disodium hydrogen phosphate and was used as supporting electrolyte. All experiments were carried out at the room temperature ($25\pm1^{0}$C).

### Instrumentation

All the electrochemical measurements were carried out using a CHI-6038E electrochemical workstation (CH-Instruments – USA) coupled with a conventional three-electrode system. The poly (L-Arginine) MCPE or BCPE is used as working electrode, a platinum wire as auxiliary electrode and the standard calomel electrode used as reference electrode.

### Preparation of BCPE

BCPE was prepared by using the mixture that is 70% graphite powder and 30% silicone oil. These two components are thoroughly mixed by hand in an agate mortar using a pestle to get a homogenous paste. Formed paste was then packed into a cavity of Teflon tube having a copper wire to provide an electrical contact with the external circuit.

### Preparation of Poly (L-Arginine) MCPE

The packing of paste was same as that BCPE. Electro polymerization of L-Arginine at BCPE was performed in 0.2 M PBS of pH 8.0 containing $1\times10^{-3}$ M L-Arginine by using CV technique. A satisfactory polymer growth was achieved by applying potential between - 0.2 to 1.6 V at a scan rate $0.1Vs^{-1}$ continuously for 10 cycles as shown in Fig.2. After polymerization, the electrode has thoroughly washed with distilled water and used for further electrochemical analysis.

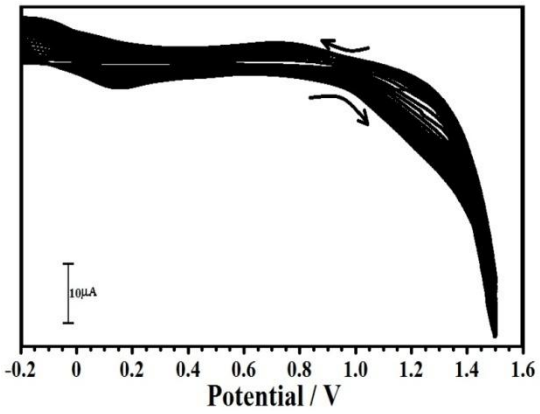


**Figure2.** *Electro polymerization of L-Arginine at BCPE*

## Results and Discussion

### Surface Morphology of BCPE and Poly (L-Arginine) MCPE

The morphological characteristics of the surfaces of BCPE and poly (L-Arginine) MCPE was done by using FESEM technique, which is one of the technique employed to study the surface morphology of thin films. It can be clearly seen from the Fig.3a the FESEM image of BCPE, which shows irregularly shaped flakes of graphite.

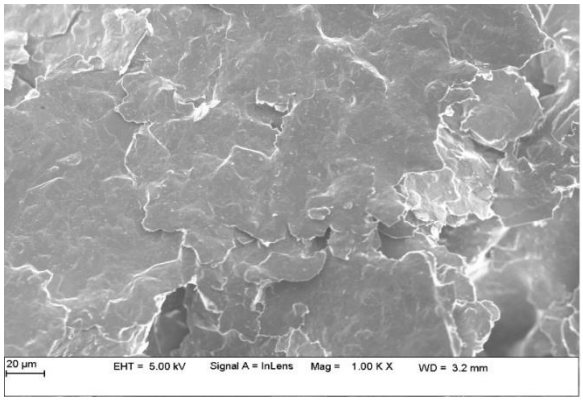


**Figure3 (a).***FESEM image of BCPE*

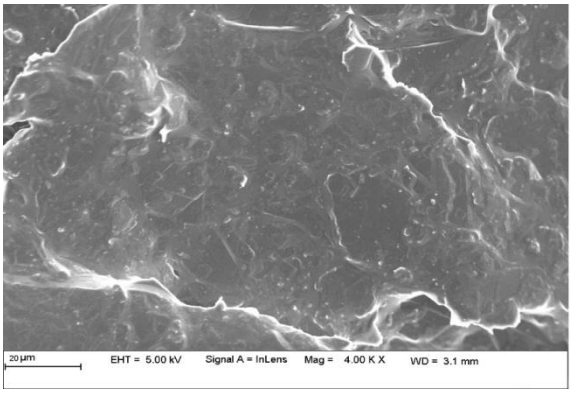


**Figure3 (b).***FESEM image of poly (L-Arginine) MCPE*

Fig.3b shows the FESEM image of MCPE, which is having a smooth, homogenously mixed poly (L-Arginine) with the graphite flakes.

## Electrochemical Response of ANT at Poly (L-Arginine) MCPE by CV and DPV Technique

To elucidate the performance of poly (L-Arginine) MCPE towards the electrochemical response of ANT in 0.2 M PBS of pH 7.0 at a scan rate 0.1 $Vs^{-1}$ was done by comparing with the BCPE under the same identical condition using CV technique.

As shown in Fig.4 the electrochemical response of ANT at BCPE was very poor (solid line), but at poly (L-Arginine) MCPE, it shows a good oxidation peak potential with high current response (dashed line) than that of BCPE. From this it can be clearly conclude that the electrochemical response of ANT enhanced by poly (L-Arginine) MCPE.

The electrochemical behaviour of ANT at poly (L-Arginine) MCPE, in 0.2 M PBS of pH 7.0 at scan rate 0.1 $Vs^{-1}$ was studied by using DPV technique.

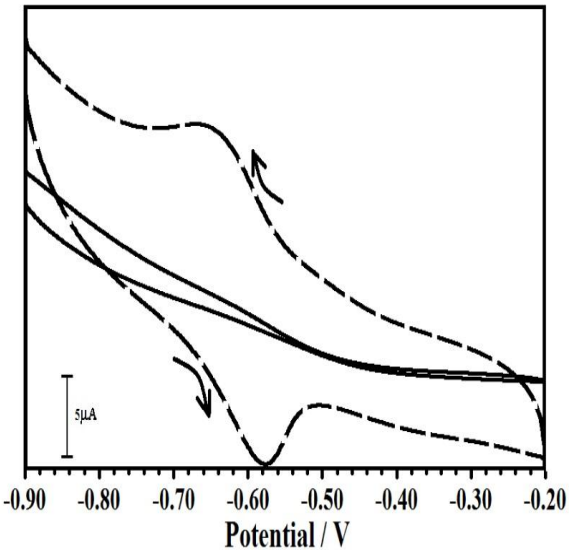


**Figure6.** *Cyclic voltammograms of electrochemical poly(L- Arginine) MCPE with $1\times10^{-3}$ M ANT (dashed line), and without ANT (solid line) in 0.2 M PBS of pH 7.0, at the scan rate 0.1 $Vs^{-1}$*

Fig.5 depicts the differential pulse voltammograms of electrochemical behaviour of ANT at poly (L-Arginine) MCPE. At BCPE, peak with low response was appeared, but at the poly (L-Arginine) MCPE, the high response peak was appeared. This result proves that the electro oxidation of ANT enhanced by poly (L-Arginine) MCPE by DPV technique.

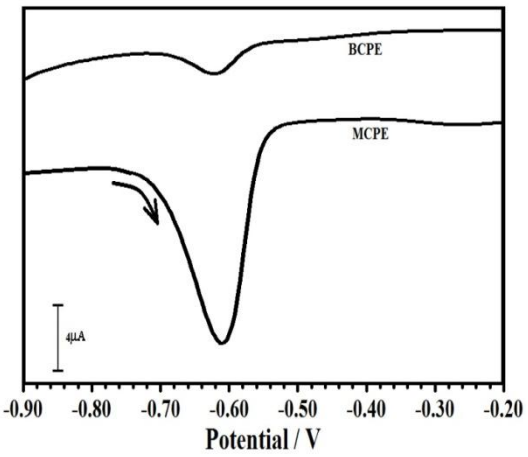


**Figure5.** *Differential pulse voltammograms of electrochemical response of $1\times10^{-3}$ M ANT at poly (L-Arginine) MCPE in 0.2 M PBS of pH 7.0, at the scan rate 0.1 $Vs^{-1}$*

## Electrochemical Response of ANT

Fig.6 shows the CVs of the oxidation of ANT in 0.2 M PBS of pH 7.0 at poly (L-Arginine) MCPE with ANT (dashed line) without ANT (solid line) was recorded by using CV technique. It can be clearly indicates that the in the absence of ANT oxidation peak does not appeared but in the presence of ANT at the poly (L-Arginine) MCPE enhanced oxidation peak appeared with the high current sensitivity. Thus it confirms that the performance of poly (L-Arginine) MCPE.

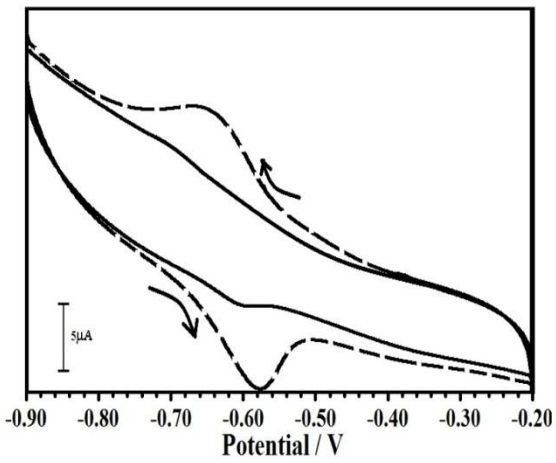


**Figure6.** *Cyclic voltammograms of electrochemical response of ANT ($1\times10^{-3}$M) at BCPE (solid line), and MCPE (dashed line) in 0.2 M PBS of pH 7.0, at the scan rate 0.1 $Vs^{-1}$*

## Effect of Variation of Sweep Rate

The CVs of the electrochemical response of the ANT in 0.2 M PBS of pH 7.0 at a poly (L-Arginine) MCPE at a various scan rate ranging from 0.1- 0.3 $Vs^{-1}$ as shown in Fig. 7a. When scan rate has been increased, peak current also increased was been observed in the Fig.7a. From

the plot of $I_{pa}$ vs. scan rate (Fig.7b) the linear relationship obtained between the peak current and scan rate, and the linear regression equation is represented as Ipa (μA) = 0.162 +4.922 v (Vs-1) with a correlation coefficient 0.9996.

This illustrates that the process is adsorption controlled [21].

Fig.7c shows the plot of logarithm of scan rate vs. $E_{pa}$ shows a linear relationship at scan rate from 0.1- 0.3 $Vs^{-1}$.

The regression equation is expressed as Epa (V) = 0.081 log v + 0.7303 with a correlation coefficient 0.9965.

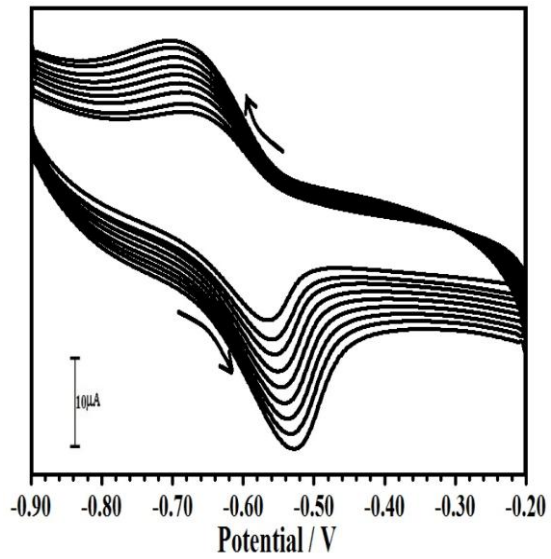


**Figure7(a).** *Cyclic voltammograms of the electrochemical behaviour of 1× $10^{-3}$M ANT at a different scan rate by using poly (L-Arginine) MCPE 0.2 M PBS of pH 7.0.*

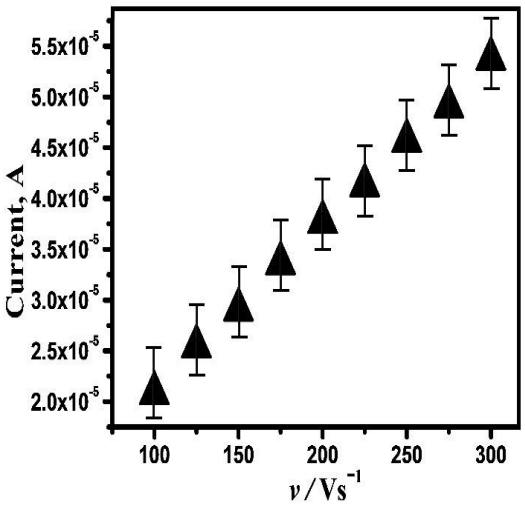


**Figure7(b).** The graph of scan rate vs. $I_{pa}$.

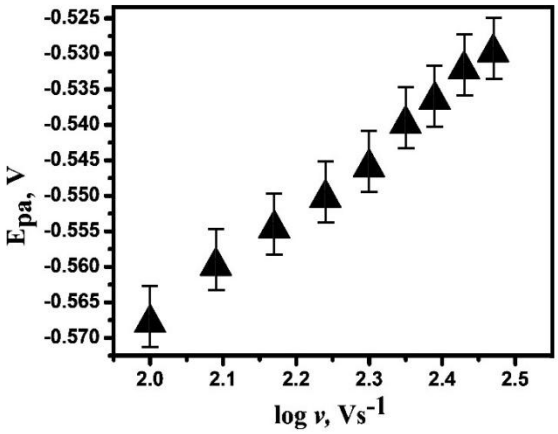


**Figure7 (c).** *The graph of log scan rate vs. $E_{pa}$*

## Effect of pH

The pH of a solution affects the electrochemical response of ANT at poly (L-Arginine) MCPE by shifting the potential towards the negative or positive direction. Fig.8a shows the CVs of the electrochemical behaviour of ANT at poly (L-Arginine) MCPE at a scan rate 0.1 $Vs^{-1}$ in 0.2 M PBS of different pH range from 6.5- 8.0. The plot of $E_{pa}$ vs. pH (Fig.8b) gives the linear relationship and the linear regression equation is presented as Epa (V) = -0.0665 pH - 0.1244. From the plot of $E_{pa}$ vs. pH the slope obtained is -0.066 which is very close to the theoretical value -0.0599 [22].

This indicates that the equal number protons and electrons involved in the electro oxidation of ANT. From the plot of $I_{pa}$ vs. pH as shown in Fig. 8c when pH increases peak current increases, after 7.0 pH the peak current decreased. From these results, the optimum 7.0 pH was considered for further analysis.

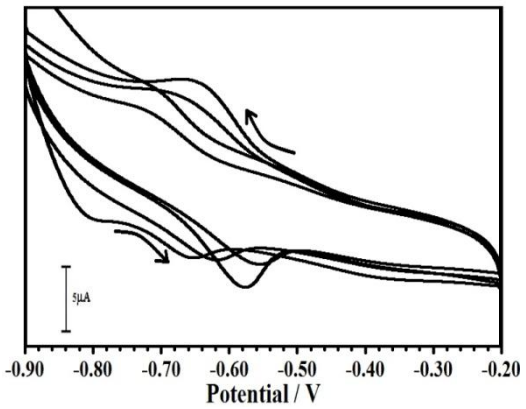


**Figure8(a).** *Cyclic voltammograms of electrochemical response of 1×$10^{-3}$M ANT at poly (L-Arginine) MCPE, varying with pH range from 6.5 - 8.0, at the scan rate 0.1 $Vs^{-1}$.*

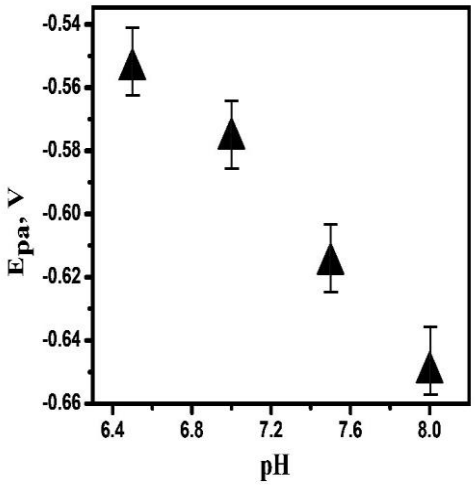


**Figure8 (b).***The graph of pH vs. Epa*

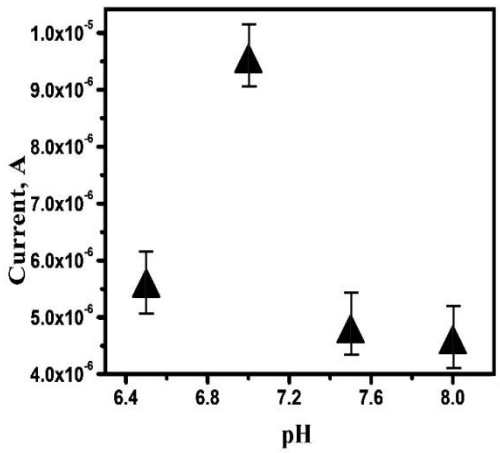


**Figure8 (c).***The graph of pH vs. $I_{pa}$.*

## Effect of ANT Concentration

The electrochemical oxidation of ANT carried out at poly (L-Arginine) MCPE using CV technique with varying an ANT concentration range $6.0 \times 10^{-6} – 1.0 \times 10^{-4}$ M in 0.2 M PBS of pH 7.0 at a scan rate 0.1 $Vs^{-1}$ to detect a low concentration of ANT.

The graph of $I_{pa}$ vs. concentration of ANT plotted was shown in Fig.9. As a concentration of ANT increases, the peak current also increases.

The expected linearity was obtained and the linear regression equation expressed as $I_{pa}$ (µA) = 0.053 + 0.994 with the correlation coefficient 0.9974. Using the equation LOD = 3S/M and LOQ = 10S/M [23], where S is the standard deviation of blank and M is slope of calibration plot, LOD and LOQ were calculated. The calculated LOD and LOQ are $4.7 \times 10^{-6}$ M and $1.5\times 10^{-5}$ M respectively.

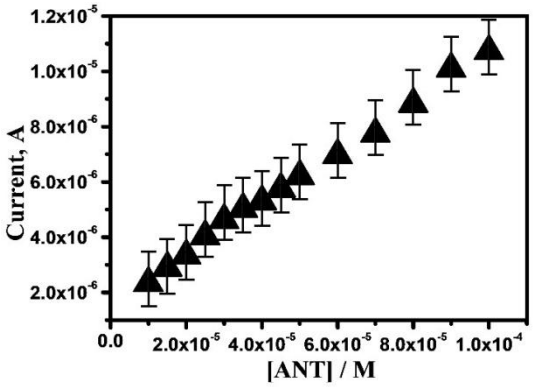


**Figure9.***The graph of concentration of ANT vs. $I_{pa}$*

## Reproducibility, Repeatability, Stability

To analyse the stability of the poly (L-Arginine) MCPE, the successive 30 cycles was scanned in the presence of $1 \times 10^{-3}$ M M ANT in 0.2 M PBS of pH 7.0 at poly (L-Arginine) MCPE by CV technique. The percentage degradation was calculated by the equation percentage degradation = $I_{pn} / I_{p1}$ [24], where $I_{p1}$ and $I_{p1}$ are last and first cycle anodic peak current respectively and the calculated degradation is 97% .

The repeatability of poly (L-Arginine) MCPE for $1 \times 10^{-3}$ M ANT in 0.2 M PBS of pH 7.0 was carried out by a series of repetitive measurements was taken. The calculated relative standard deviation (RSD) for four measurements is 3.11 %. The reproducibility of the poly (L-Arginine) MCPE was examined by fabricating the MCPE separately in an identical condition and recording CVs for $1 \times 10^{-3}$ M ANT in 0.2 M PBS of pH 7.0. Expected reproducibility obtained with RSD of 3.08 %. These are all results clearly indicates that the poly (L-Arginine) MCPE has a good reproducibility, repeatability, and stability.

## Conclusion

In this study, a simple, sensitive, and selective poly (L-Arginine) MCPE for the electrochemical analysis of ANT by using CV technique was developed. The modified electrode shows a good electro catalytic activity towards the electrochemical oxidation of ANT. The developed MCPE also shows a high current sensitivity, good stability, high speed for the detection of ANT. A good linear range with low detection limit for ANT was obtained at poly (L-Arginine) MCPE. Finally, simple, low cost modification procedure was developed for the detection of ANT.

## ACKNOWLEDGEMENT

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