

Poly (threonine) Modified Carbon Composite Electrode as Sensor for Amoxicillin Determination

Nagaraja Sreeharsha^{1,2,*}, Mallikarjun Telsang³, Girish Meravanige Basavarajappa⁴, Swati Pund⁵, Ranjith Kumar Karnati⁶

¹ Department of Pharmaceutical Sciences, College of Clinical Pharmacy, King Faisal University, Al-Ahsa 31982, Saudi Arabia;

² Department of Pharmaceutics, Vidya Siri College of Pharmacy, Off Sarjapura Road, Bangalore 560035, Karnataka, India

³ Department of Surgery, College of Medicine, King Faisal University, Al-Ahsa 31982, Saudi Arabia;

⁴ Department of Biomedical Sciences, College of Medicine, King Faisal University, Al-Ahsa 31982, Saudi Arabia;

⁵ Nanomedicine Laboratory, Department of Biosciences and Bioengineering, Indian Institute of Technology-Bombay, Mumbai 400076, India;

⁶ Department of Chemistry, College of Science, King Faisal University, Al-Ahsa 31982, Saudi Arabia

*E-mail: mvtelsang@kfu.edu.sa, sharsha@kfu.edu.sa

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The poly(threonine) carbon composite sensor was concentrated as a totally special sensor for the assurance Amoxicillin (AM). The behavior of AM at the electrode surface was researched utilizing electrochemical cyclic voltammetry (CV) and field emission scanning electron microscopy (FE-SEM). Electrochemical investigations uncovered that the projected sensor showed a significant benefit, involving high operative surface area, plentiful reactive spots and outstanding electro-catalytic action for the AM oxidation. In the ideal circumstances, the sensor showed a fine linear response towards the oxidation of AM in the concentration range from 0.10–16.0 μM . The assessed limit of detection and quantification were found to be 0.12 μM and 0.45 μM for AM, respectively. This sensor showed a good sensitivity, steadiness, selectivity, and reproducibility, proposed that the prepared sensor was a capable one for the concurrent assurance with dopamine (DA) and superb recuperation and without the impedances of existing together substances.

Keywords: Amoxicillin; Dopamine; polymerization; Electroanalysis.

1. INTRODUCTION

AM (α -amino-hydroxy benzyl penicillin) might be a wide range penicillin arranged under the β -lactam class of anti-toxins. It is a semi-synthetic antibiotic got from a precursor molecule called 6-

aminopenicillanic acid. AM most by and large utilized β -lactam anti-toxin for the cure of bacterial diseases like nose, ear, skin, throat, and lower plot brought about by helpless microbes [1–3]. it's higher assimilation capacity than another β -lactam anti-microbials [4]. The norm and unwavering quality of prescription on their measurement, amount and hence the method of use. In writing, a few scientific techniques are operated in the measurable assurance of AM like LC/fluorescence [5], liquid chromatography-tandem mass spectrometry [6], UV spectrophotometry [7, 8], High-resolution mass spectrometry [9], capillary electrophoresis [10], high-performance liquid chromatography technique coupled with tandem mass spectrometry [11] and ultra-high-performance liquid chromatography-tandem mass spectrometry [12]. Then again, electrochemical strategy gives a simple, ease, exact, and rapidity stage for the recognition of biotic compounds of medical attention [13-21]. The sorts of carbon sensors like carbon paste, screen-printed carbon, glassy carbon, carbon fiber, and carbon films are utilized generally in the electrochemistry as a sensing tool [22-27]. These sensing tools have a few benefits, involving ease, generally sensitive electrochemistry, broad potential gap, and electro-catalytic action for an assortment of oxidation/reduction responses [28-31]. Carbon composite paste electrode (CCPE) is the maximum popular electrode. This can be made by mixing graphitic and carbon nanotubes [32-37]. The chemically fabricated CCPEs have acquired a lot of consideration in electrochemical field [38-42]. Modified electrodes are of speeding up interest in modern electroanalysis, as they grant the gathering of analytes on the electrode surface. they're additionally effortlessly prepared by adding the modifier straightforwardly to a CCPE [43-52]. This pre concentration step expands the sensitivity and selectivity of the assurance. In this paper, we will examine the application of poly(threonine) as modifier in the development of a CCPE for the assurance of AM in nanomolar concentrations. The advantages of utilizing a CCPE incorporate the availability of a wide potential range for analysis, effectively renewable surface, and simplicity of modification.

2. MATERIALS AND METHODS

2.1. Reagents

Compounds used in phosphate buffer solution (PBS), AM, Paraffin oil, Graphite powder and DA were bought from MERCK chemicals and were utilized without further refinement. Standard solution of AM was prepared in distilled water and DA was prepared in perchloric acid. AM real sample was collected from a local pharmacy store.

2.2. Apparatus

The electrochemical estimations were achieved using a potentiostat or galvanostat electrochemical system having tri-electrode assembly. Here, CCPE and PTNMCCPE are the working electrodes, platinum wire is the auxiliary electrode and saturated calomel electrode is the reference electrode.

2.3 Preparation of the electrode

The frame of the CCPE was a Teflon rod having an opening of 3 mm inner diameter. Electrical connection was finished using a copper lead over the focal point of the pole. Fabricated CCPE was prepared in an ordinary design by altogether hand-mixing, carbon nanotubes (20%), graphite powder (50%) and silicone oil (30%) in a mortar with a pestle. The fabricated electrode was stuffed into the hole of the electrode and polished with a tissue paper.

Electrochemical polymerization methods were utilized for the fabrication of poly (threonine) modified carbon composite electrode (PTNMCCPE) in PBS (pH 7.0) containing 1×10^{-3} M threonine at the expected potential opening range from -0.3 to 1.4 V in the sweep pace of 0.1 V/s (shown in Fig. 1). The peak current increment with the expanding number of cycles demonstrating that the polymeric film was growing on the electrode surface. The peak current was greatest for 10 cycles, after it diminishes. Subsequently we picked 10 cycles as the ideal output number, after 10 cycles, the outside of the electrode was cleaned with refined water to isolate the physically formed substances.

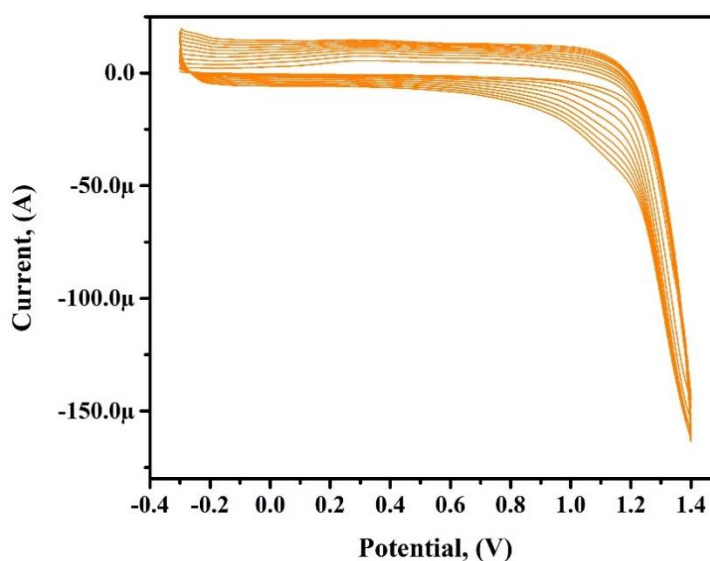


Figure 1. CVs for the electrochemical polymerization of threonine on CCPE in PBS of pH 7.0 at 0.1 V/s scan rate.

3. RESULT AND DISCUSSION

3.1 Morphological studies

Surface morphology of the BCCPE and PTNMCCPE was examined utilizing FESEM. Fig. 2 shows the FESEM picture of BCCPE (a) and PTNMCCPE (b). The surface of BCCPE shows irregular arrangements of graphite and carbon nanotube. Whereas, the PTNMCCPE shows that the uniform surface which shows the surface of the BCCPE was generally covered with polymer film of TN. This shows that the CCPE successfully modified with polymerization.

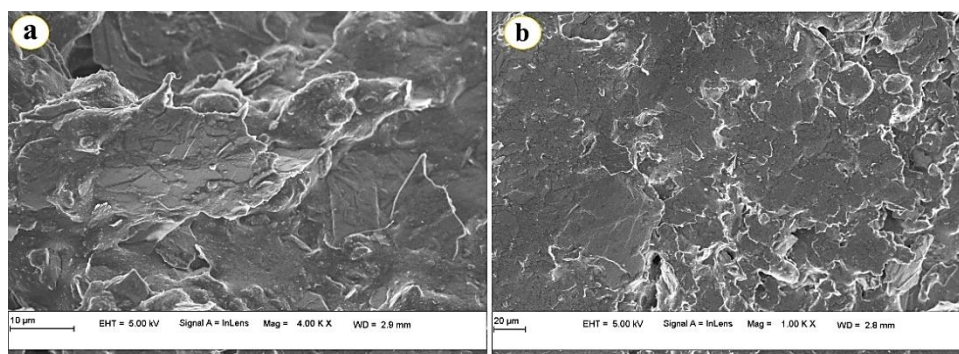


Figure 2. The FESEM descriptions of (a) BCCPE and (b) PTNMCCPE.

3.2 Analysis of electrode surface area

CVs of 1mM $K_4 [Fe (CN)_6]$ redox couple was implemented to analysis on a PTNMCCPE (line a) and BCCPE (line b) are appeared in Fig. 3. It is obvious that the PTNMCCPE shows stable improvement in the peak current, demonstrating that the electro-active spots of CCPE amplified in the surface modification by the electrochemically polymerized TN. The greatest peak current at the PTNMCCPE ($I_{pa} = 30.15 \mu A$) in contrast with BCCPE ($I_{pa} = 14.61 \mu A$) is credited to electro-catalytic action and improvement in the active-surface area due to the surface modification. The active-surface area of the working electrodes was projected using the Randles–Sevcik equation [53, 54]:

$$I_{pa} = 2.69 \times 10^5 n^{3/2} A C_o D^{1/2} \nu^{1/2}$$

Where, n is the number of electrons, I_{pa} is the Anodic peak current, A is the active surface area, C_o is the concentration of the analyte, D is the diffusion coefficient, ν is the scan rate. The electro-active surface area is highest for PTNMCCPE (0.0449 cm^2) in contrast to the BCCPE (0.0217 cm^2).

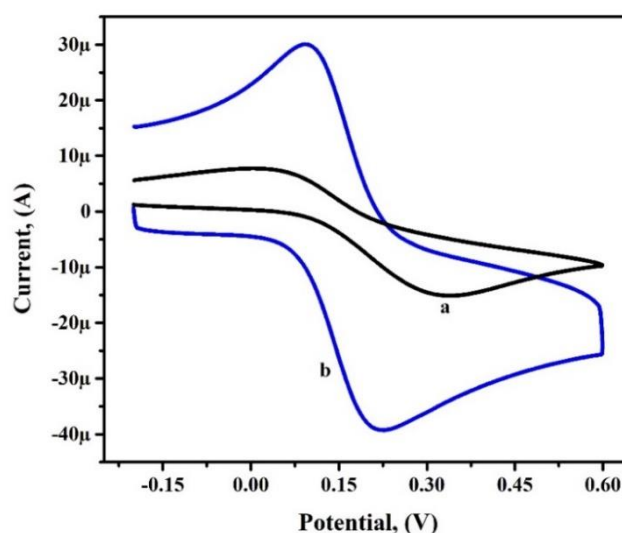


Figure 3. CVs for 1mM $K_4 [Fe (CN)_6]$ at BCCPE (a) and PTNMCCPE (c) at the scan rate of 0.1 V/s.

3.3 Electro catalytic analysis of AM

With the intension to evaluate the electrochemical behaviour of PTNMCCPE, its CV reaction was recorded in PBS of pH 7.0 containing 0.1 mM AM at 0.1 V/s. Fig. 4 depicts the CVs for BCCPE (line a) and PTNMCCPE (line c) in the presence and non-appearance (line b) of 0.1 mM AM, individually. The acquired result showed that in the examination, AM oxidation happens with an oxidation peak potential at 0.59 V, while without AM, no peak was identified. This affirms the peak fund at 0.59 is corresponds to the oxidation of AM. Moreover, CV reaction was likewise recorded for AM at BCCPE, where a feeble reaction was noticed for the oxidation of AM ($I_{pa}= 4.4 \mu\text{A}$). In opposition to the BCCPE, enhanced anodic peak obtained with the peak current of $I_{pa}= 14.31 \mu\text{A}$ at PTNMCCPE affirms the improved catalytic activity of PTNMCCPE towards the electro-oxidation of AM. The event of just anodic peak in the forward examining and the shortfall of peak in the in the reverse scanning at BCCPE as well as in PTNMCCPE signifies that the oxidation of AM is irreversible at both the electrodes.

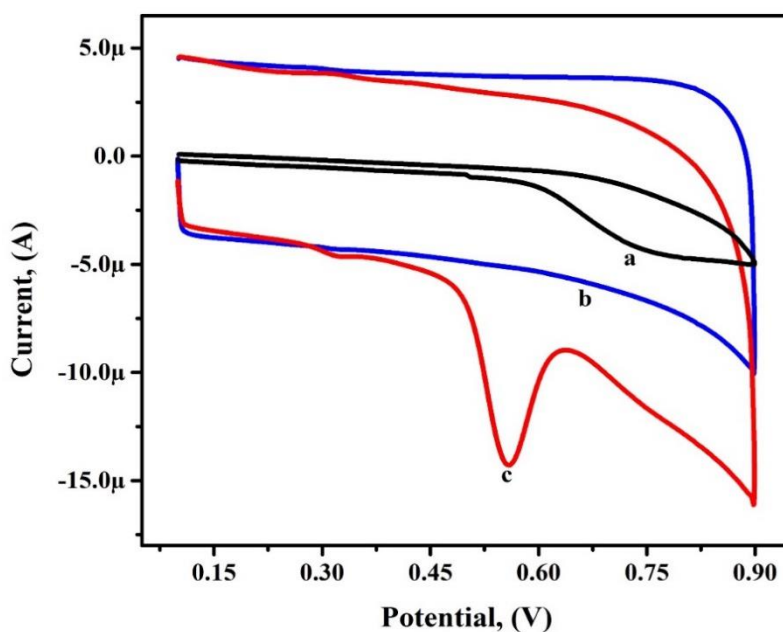


Figure 4. CVs for (a) BCCPE and (c) PTNMCCPE in the (b) absence of AM at the scan rate of 0.1 V/s.

3.4 Influence of pH

The impact of pH to the oxidation peak current and oxidation peak potential was tested in PBS of different pHs (6.0 to 8.0) at the concentration of 0.1 mM AM. Since the pH of the arrangement may specified the electrochemical action of the analyte. Fig. 5a outlines the CV reaction of the analyte arrangement at different pH esteems. In this examination, the outcomes got affirm that in the favored pH range, peak potential consonant to the reduction process at PTNMCCPE is pH dependent and the peak current attains its summit at pH 7.0. Thus, pH 7.0 was picked as the ideal pH for additional

examinations. The relationship among the PBS pH and the oxidation potential of the concavity can be determined by the condition $E_{pa} = 0.978 - 0.058 \text{ pH}$ ($R = 0.909$) (Fig. 5b). The slope of linear segment got was 0.058 V/pH , which is in near concurrence with the theoretic value (0.059 V/pH) expected for the transfer of equivalent number of protons/electrons at electrode surface [49-52].

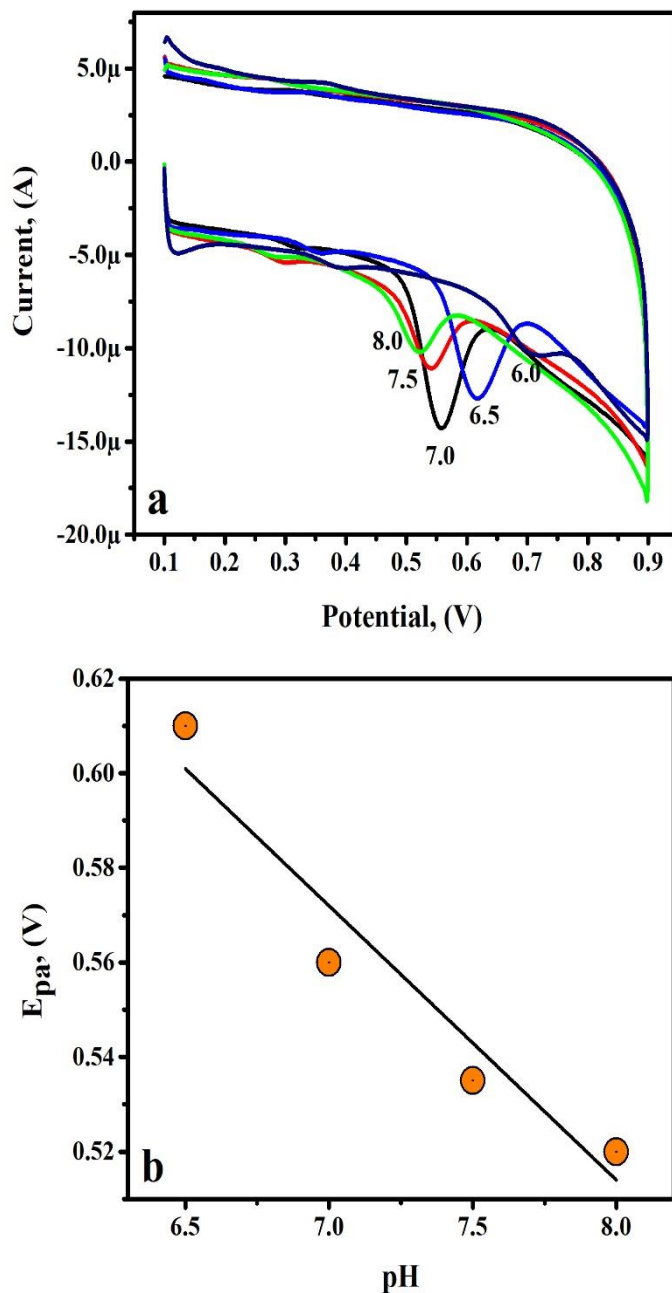


Figure 5. CVs for AM in different PBS pHs (6.0 to 8.0) at the scan rate of 0.1 V/s. **(b)** The plot of pH versus E_{pa} .

3.5. Influence of Scan rate

CV was utilized to determine the impact of scan rate to the AM oxidation. As demonstrated in Fig. 6a, the peak current of 0.1 mM of AM on PTNMCCPE was documented by scan rates from 0.1 – 0.3 V/s. It was realized that on increasing the scan rate the anodic peak current was likewise gradually improved. In Figure. 6b and 6c, the plots of log peak current versus log scan rate and peak current vs. square root of scan rate display a fine linear relationship and the linear regression equations were $\log I_{pa}(A) = -3.990 + 0.643 \log v \text{ V/s}$ ($R = 0.998$) and $I_{pa}(A) = -0.923 + 10.330 v^{1/2} \text{ V/s}$ ($R = 0.994$). These outcomes suggests that, the quasi-reversible oxidation interaction of AM on the surface of PTNMCCPE was constrained by adsorption process.

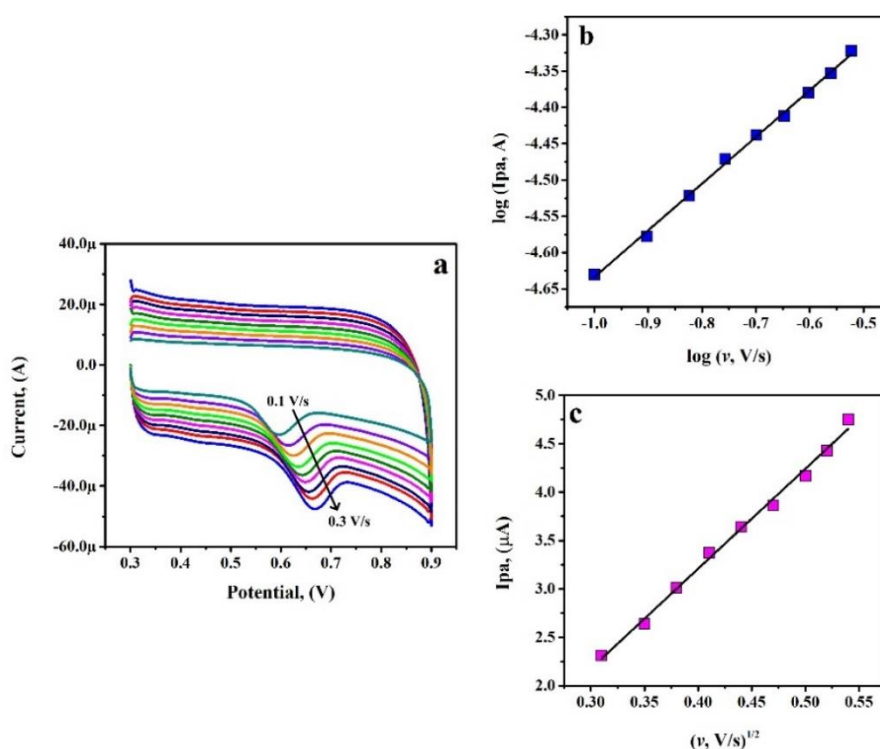


Figure 6. (a) CVs for AM in PBS of pH 7.0 at PTNMCCPE with dissimilar scan rate from 0.1 to 0.3 V/s. (b) The plot of log peak current vs. log scan rate. (c) The plot of scan rate current vs. root scan rate.

3.6. Calibration curve of AM

The sensitivity is one of the fundamental properties and the preminent benefit of the proposed sensor. Along these lines, to analyze the sensitivity the electrocatalytic oxidation of AM of different concentration was performed on PTNMCCPE by CV. In Fig. 7, elucidates the calibration plot of peak current vs. [AM], ranging from 0.10–16.0 μM , espied to have linearity resulting with equation $I_{pa} (A) = 5.935 \times 10^{-6} + 0.147 C$ ($R^2 = 0.9933$). The following IUPAC equation evaluated the detection limit and quantification limit relations,

$$\text{LOD} = 3\sigma/d \quad (4)$$

$$\text{LOQ} = 10\sigma/d \quad (5)$$

Hither, ' σ ' is the standard deviation assessed for the blank solution and ' d ' is the slope of the calibration plot of AM. The assessed limit of detection and quantification were 0.12 μM and 0.45 μM for AM. The limit of detection of PTNMCCPE was contrasted with previously announced works in Table 1 [55-60].

Table 1. Contrast of reported AM sensors with present sensor.

Electrode	Technique	LOD (μM)	Reference
Gold-palladium nanoparticles aided electrochemically reduced graphene oxide on glassy carbon electrode	SWV	9.00	[55]
nickel–curcumin complex modified carbon paste electrode	Amperometry	5.00	[56]
ferrocenedicarboxylic acid multi wall carbon nanotubes paste electrode	SWV	0.0089	[57]
multiwalled carbon nanotubes modified glassy carbon electrode	CV	0.200	[58]
Poly(acridine orange) modified glassy carbon electrode	DPV & SWV	0.00018 & 0.0155	[59]
carbon nanotubes/gold nanoparticles/screen printed electrode	ADSV	0.015	[60]
PTNMCCPE	CV	0.120	Present work

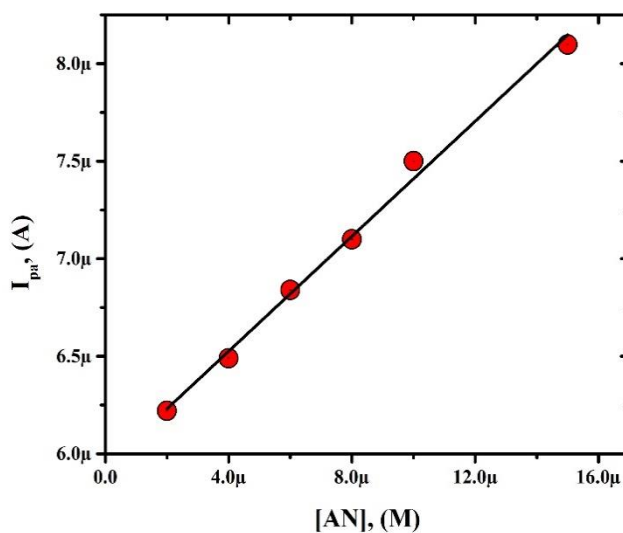


Figure 7. The plot of concentration of AM v/s Current.

3.7 Simultaneous analysis of AM with DA

The simultaneous examination of AM with DA was finished utilizing the CV technique at PTNMCCPE (line a) and BCCPE (line b) in PBS as demonstrated in Fig. 8. The fabricated sensor discloses well and discrete oxidation peak corresponds to AM with DA in the nonappearance of a contextual current at the oxidation peak potentials of 0.6 V and 0.34 V, respectively. Besides, at BCCPE the discrete peak to peak split for AM with DA isn't vibrant. This result determines that, PTNMCCPE shows a selective, and sensitive AM investigation in the DA occurrence.

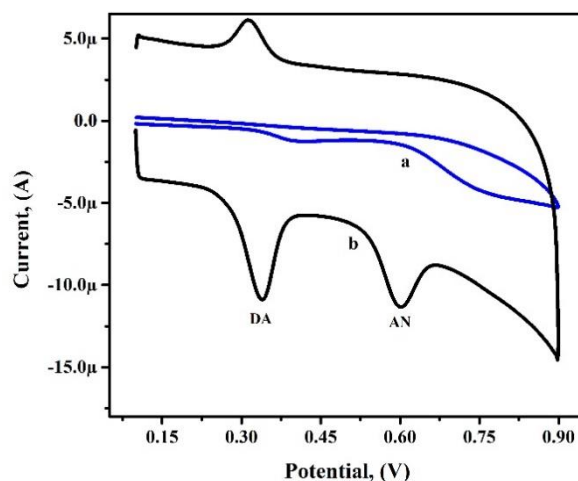


Figure 8. CVs for AM and DA in PBS of pH 7.0 at BCCPE and PTNMCCPE at 0.1 V/s scan rate.

3.8 Reproducibility and Stability of the sensor towards AM

CV technique was utilized for the assurance of reproducibility and stability of the projected sensor to AM at ideal circumstances. PTNMCCPE shows good reproducibility for five sequential sequences with the relative standard deviation (RSD) of 3.6 % and the stability of 94%, and this outcome documents that the proposed electrochemical sensor is having finest reproducibility and stability towards AM.

3.9 Pharmaceutical sample Analysis

The explored outline was implemented for the assessment of AM at PTNMCCPE in a medicinal sample. The determination of concentration and amount of AM was finished via standard addition technique. The information was recorded in Table. 2 and showed that the fabricated electrochemical sensor exhibits a robust catalytic reply for AM in the occurrence of supplementary biologically active fractions in the real sample with a fine recovery of 99.52% -100.61%.

Table 2. Recovery results of AM in Pharmaceutical medicine.

Sample	Added (μM)	Found (μM)	Recovery (%)
Pharmaceutical sample	10.00	10.48	100.40
	20.00	20.01	100.61
	30.00	29.85	99.52

4. CONCLUSIONS

This work depicts the preparation of PTNMCCPE for delicate assurance of AM utilizing CV. PTNMCCPE exhibits predominant electrocatalytic movement for the oxidation of AM at an ideal pH of 7.0 in 0.2 M PBS. The LOD and LOQ were discovered to be 90.12 μM and 0.45 μM individually. The PTNMCCPE gives great repeatability, reproducibility and stability. The electrode procedure is discovered to be adsorption controlled. The concentration and pH impact were seen to be linear in room temperature. The recovery results got in the real sample examination shows that the proposed strategy can be utilized for the electrochemical detecting of AM and the modified sensor can be convincingly utilized for simultaneous analysis of AM and DA.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results

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