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Determination of Terazosin by using Poly (Congo red) Modified Carbon Paste Electrode

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Abstract- A simple, sensitive and selective electrochemical method is developed for the determination of terazosin (TR) by using cyclic voltammetry and differential pulse voltammetry. A poly congo red carbon paste electrode (poly CR/CPE) based sensor was successfully fabricated by the electro polymerization process by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). This modified carbon paste electrode exhibited a good electro catalytic activity towards the resolution of terazosin in 0.1M phosphate buffer solution (PBS) at pH 7.0. The effect of pH, scan rate, concentration of Terazosin were studied by using congo red modified CPE. The modified electrode showed a good detection limit of 7.3 µM over the linear dynamic range of 1.76×10^{-5} M to 3.33×10^{-5} M, which is better than many reported methods in the literature. The prepared poly (CR) modified electrode exhibited good stability, high sensitivity, better reproducibility, low detection limit towards the determination of Terazosin(TR). Finally, the electrochemical oxidation of TR at the surface of poly CR/ CPE was employed for the determination of TR in real sample analysis.

Keywords- Terazosin(TR), Congo Red(CR), Cyclic voltammetry(CV), Differential pulse voltammetry (DPV)

1. INTRODUCTION

Terazosin hydrochloride is 2-[4-(2-tetrahydrofuranyl carbonyl]-1-piperazinyl-6,7-dimethoxy-4-quinazolinamine monohydro-chloride dehydrate, (TR) (Fig. 1). is classified as a quinazoline and it is similar to doxazosin and prazosin [1]. It is a highly selective alpha adreno receptor antagonist [2] and an effective drug for hypertension by relaxing veins and arteries. It is used in the treatment of hypertension and for the suggestive treatment of urinary obstruction caused by benign prostatic hyperplasia (BPH) by relaxing the muscles of the bladder and prostate [3-5]. The main side effects of TR include dizziness, drowsiness, headache, constipation, loss of appetite, tiredness, nasal congestion or dry eyes, but they generally go away after only a few days of use. After oral administration TR is very rapidly and completely adsorbed from the gastrointestinal tract [6]. The effectiveness of terazosin as an antihypertensive is reported in the literature [7-9] and the TR pharmacokinetics were shown to be linear in the range of 0.1–7.5 mg orally and 1–5 mg intravenously [10]. It undergoes wide hepatic metabolism and the major route of elimination is via the biliary tract [11]. Several methods for the determination of this drug have been reported in the literature, including, high performance liquid chromatography [12-17], spectrophotometry [18,19], spectrofluorimetry [20,21] and voltammetric methods [22,23]. Electro Analytical methods have been reported for the determination of TR in bulk form, pharmaceuticals and human plasma. Numerous dyes act as synthetic electron donors such dyes can easily undergo electropolymerisation from electrolytic aqueous solution forming uniform redox dynamic layer.

The above mentioned methods are time-consuming, require sample pretreatment step and long analysis times and require sophisticated relatively expensive instruments. Electrochemical measurements can overcome those shortages due to the advantages of rapid and simple operation, easy application, low cost, high sensitivity and ability to real-time monitor analytes in low concentrations and play a significant role in drug quality control in pharmaceutical dosage forms and biological fluids [24]. Therefore, the development of sensitive, simple, fast and reliable method for the determination of Active Pharmaceutical Ingredients (API) in drugs is of great attention. To the best of our knowledge few electrochemical methods are reported for the determination of TR [25-26]. Congo red [3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid)] is an azoic compound synthesized by Paul Böttiger is used to stain microscopic prepares, especially as a cytoplasm and erythrocyte stain.

In this study, a novel electrochemical sensor was constructed by electropolymerizing CR film on CPE and used for the determination of TR at low levels. Compared with the bare CPE the poly (CR)/CPE could remarkably improve the electrochemical response to TR. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were applied to thoroughly investigate the electrochemical behaviors of TR. The primary objective of this work is to

develop a highly sensitive and selective interface for electrochemical determination of TR in the routine analysis.

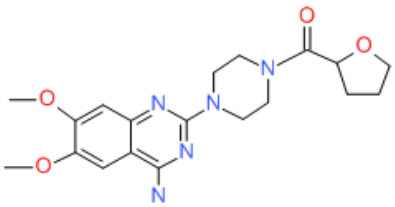


Fig. 1. Terazosin structure

2. EXPERIMENTAL

2.1. Chemicals

Terazosin, sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4), fine graphite powder and silicon oil were supplied by Merck (Darmstadt, Germany) and Sigma-Aldrich Laboratories Pvt. Limited, Mumbai and used with no further purification. Congo red was purchased from Fine Laboratories Pvt. Limited, Mumbai, India. All other chemical reagents used were of analytical grade. The supporting electrolyte used was a phosphate buffer solution (PBS) of pH 7.0 for all the measurements. All the solutions were prepared using Millipore water.

2.2. Apparatus

Voltammetric methods were performed using with a CH-Instrument Model CHI610D (USA) potentiostat with a conventional three electrode cell, a platinum wire as a counter electrode and an Ag/AgCl (saturated KCl) as a reference electrode. A bare CPE (2.0 mm diameter) and poly (CR)/CPE was used as the working electrode and the pH values were measured with Elico Li 120 pH meter. All the experiments were carried out at the room temperature (25 $^{\circ}$C).

2.3. Preparation of bare CPE and poly (CR)/CPE

The bare CPE was prepared by hand mixing of graphite powder and silicon oil in the ratio of (70:30%) in an agate mortar to obtain a homogenous carbon paste. This carbon paste was packed into a plastic tube with the inner diameter of 2 mm. The modified CPE was prepared by the electrochemical polymerization of CR on to the surface of CPE in 0.1 M PBS of pH 7.0 containing 1.0 mM of CR with cyclic voltammetric sweeps in the potential range of 0.6 V to 1.2 V at the scan rate of 50 mvs^{-1} and then the polymerization can be carried out in 30 cycles. After the polymerization, the surface of the electrode was washed with double distilled water.

3. RESULTS AND DISCUSSION

3.1. SEM analysis of poly (CR)/CPE

Fig. 2 shows the surface morphology of bare CPE (a) and poly (CR)/CPE (b) using Scanning Electron Microscopy (SEM). The surface of the bare carbon paste electrode was shaped like the flakes of graphite. However, the poly (CR)/CPE has a characteristic regular arrangement of poly (CR) molecules on the surface of the CPE. This confirms that the CPE was coated by poly (CR) film, and leads to the increase in the surface activity of the poly (CR)/CPE.

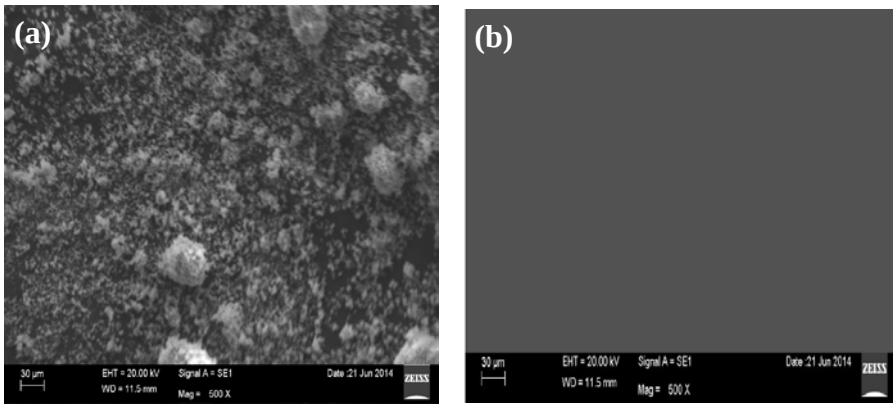


Fig. 2. SEM images of (a) BCPE; (b) Poly CR/ CPE

3.2. Electrochemical polymerization of poly (CR)/CPE

During polymerization process the oxidation peak current is directly proportional to the number of cyclic voltammetric scans representing that the electro conductive polymer film was formed on the electrode surface.

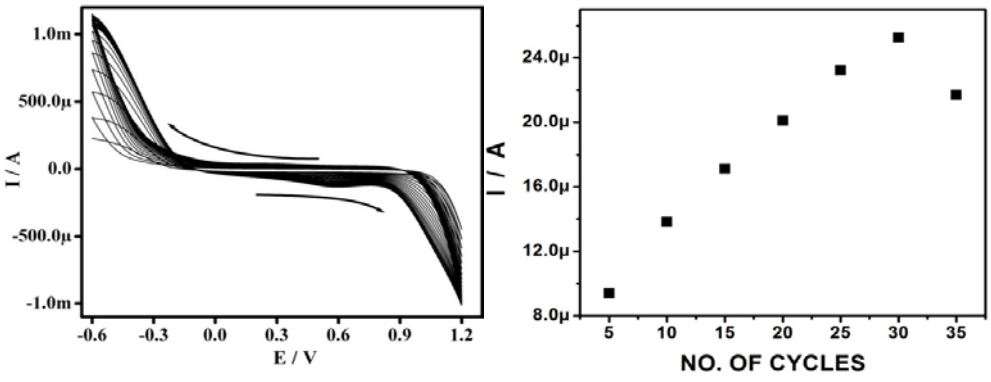
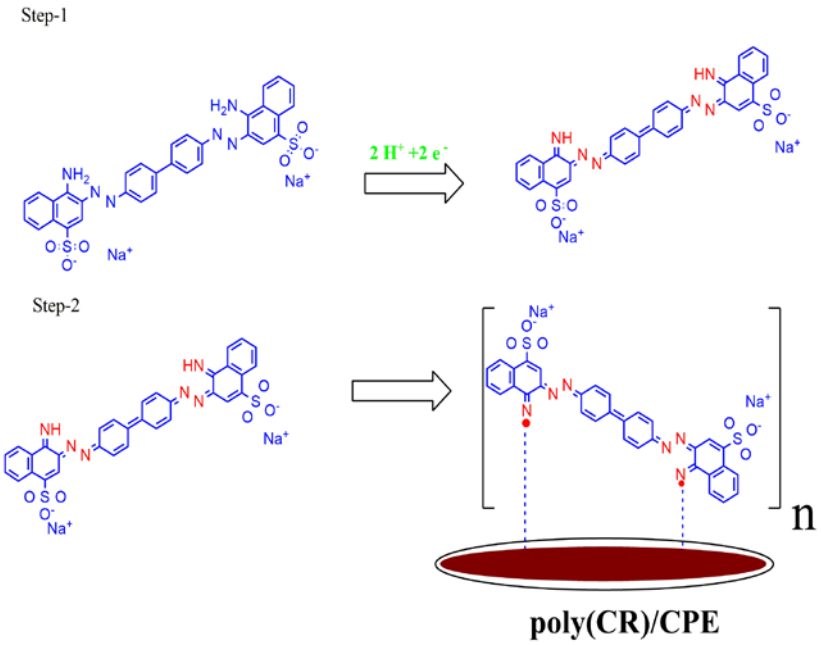


Fig. 3. (a) Cyclic voltammograms for the electrochemical polymerization of 1 mM Congo Red on a carbon paste electrode at the scan rate of 50 mVs^{-1}; (b) Dependence of the oxidation peak current of 0.025 mM TR on the number of voltammetric scans

The electropolymerisation reaction mechanism is shown in the scheme 1: In the first step, CR undergoes deprotonation and in the second step, the addition polymerization takes place between CR radical and the CPE as evidenced by (Scheme 1) [27].



Scheme 1. Mechanism for electrolytic oxidation of TR at the (poly congo red) MCPE

Fig. 3 shows that the effect of cycles of electro polymerization on the oxidation peak current (Ipa) of 25 mM Terazosin in PBS (pH 7.0). Here current response was increased up to 30 cycles and thereafter it decreases. Hence, in this study, we have chosen 30 cycles as the optimum number for the formation of a polymer film on the electrode surface area.

3.2. The electrochemical response of TR at the bare CPE &Poly (CR)/CPE

Fig. 4 Shows the Cyclic voltammogram of bare CPE (dotted line), poly(CR)/CPE using 0.025 mM TR in 0.1 M PBS (pH=7.0) at the scan rate of 50 mVs^{-1}. When compared with bare CPE, The modified CPE showed 2 folds increase in anodic currents for TR. The peak potential difference (E_P) of 53.1 mV was obtained. This is equal to 59/n mV, indicating that the same number of protons and electrons are involved in the reaction mechanism. In the similar condition our modified carbon paste electrode (thick line) exhibited an excellent sensitivity for the determination of TR.

This electro catalytic activity of poly (CR)/CPE is due to the electron releasing SO_3^{2-} ions and amine groups present on the surface of CPE. Due to the existence of electron rich groups, poly (CR)/CPE shows a good affinity towards the TR. It easily undergoes that the oxidation by exchanging the positive ions with the electrons released by the above mentioned groups

and these electron rich groups in the poly (CR)/CPE shows a good affinity towards the TR positive ions by exchanging the electrons. This concludes that the poly (CR)/CPE (Thick line) exhibits an excellent sensitivity for the determination of TR.

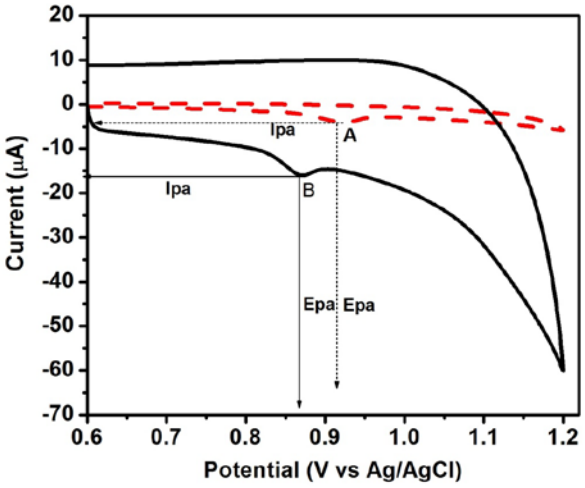


Fig. 4. Cyclic voltammograms obtained for the oxidation of 0.025 mM TR in 0.1 M PBS (pH 7.0) at BCPE (dotted line) and Poly CR/CPE (thick line) Scan rate: 50 mV/s

3.3. Effect of pH

The electrochemical oxidation of TR of the peak current and peak potential are affected by pH of the working solution. The current responses and oxidation potentials of TR at poly (CR)/CPE was investigated in the pH range from 5.5 to 8.0 of PBS by CV. By increasing the pH, the current of TR oxidation peak was increased and the maximum oxidation peak current of TR was observed in pH 7.0.

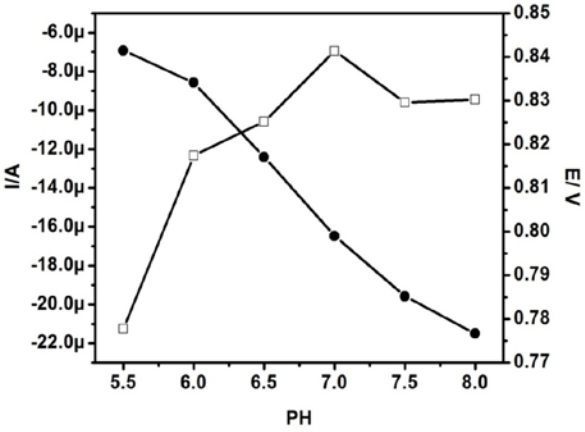


Fig. 5. Effect of pH on anodic peak current (I_{pa}) (-□-), anodic peak potential (E_{pa} (-●-) of 0.025 mM TR in 0.1 M phosphate buffer solution.

3.4. The effect of scan rate on the oxidation of TR at Poly (CR)/CPE

The effect of scan rate on the response of 0.025 mM TR in 0.1 M PBS at pH 7.0 was studied by CV using poly (CR)/CPE over a potential range of 0.6V to 1.2 V.

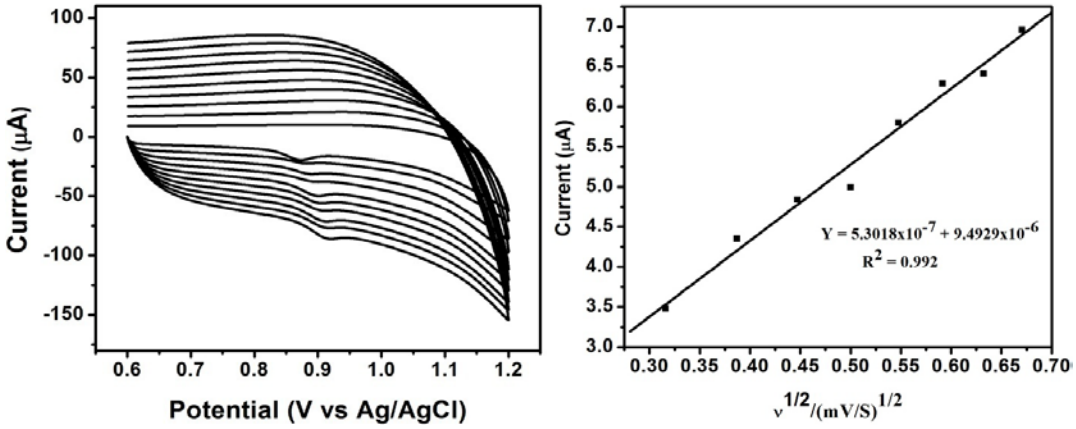


Fig. 6. (a) Graph of the effect of variation of pH of PBS in 0.025 mM TR at the scan rate 50 of mVs^{-1}; (b) Graph of the effect of variation of pH of PBS in 0.025 mM TR at square root of scan rate 50 of mVs^{-1}

The CV response for the electrochemical oxidation of TR in the presence of Poly (CR)/CPE at different scan rates between 50 and 500 mVs^{-1}. From Fig.6 It can be observed that the oxidation peak potential shifts positively with the increase of scan rate. The oxidation peak currents I_{pa} of TR increase linearly with the square root of scan rate. The linear relationship between the redox peak current and the scan rates indicate that the electrochemical oxidation of TR at the poly (CR)/CPE is an adsorption controlled process.

3.5. Analytical performance

It involves the determination of the detection limit of TR in the presence of poly (CR)/CPE. The sensitivity of electrode was employed by the using differential pulse voltammetric (DPV) technique. Fig. 7 shows the anodic peak current observed at the poly (CR/CPE) at various concentrations of TR. The linear regression equation was I_{pa}=1.829+2.655 R^2=0.993 and the diagram shows the graph between I_{Pa} vs. concentration of TR showing the linear dynamic range (LDR) from 1.76×10^{-5} M to 3.33×10^{-5} M. The detection limit of 7.3×10^{-6} M and limit of quantification of 2.4×10^{-5} M calculated as and by using the following formulae [28,29].

$$LOD=3\times SD/B \quad (1)$$

$$LOQ=10\times SD/B \quad (2)$$

Where SD is the Standard deviation, B is the slope obtained from the calibration plots. This detection limit is better than the detection limits of various literature.

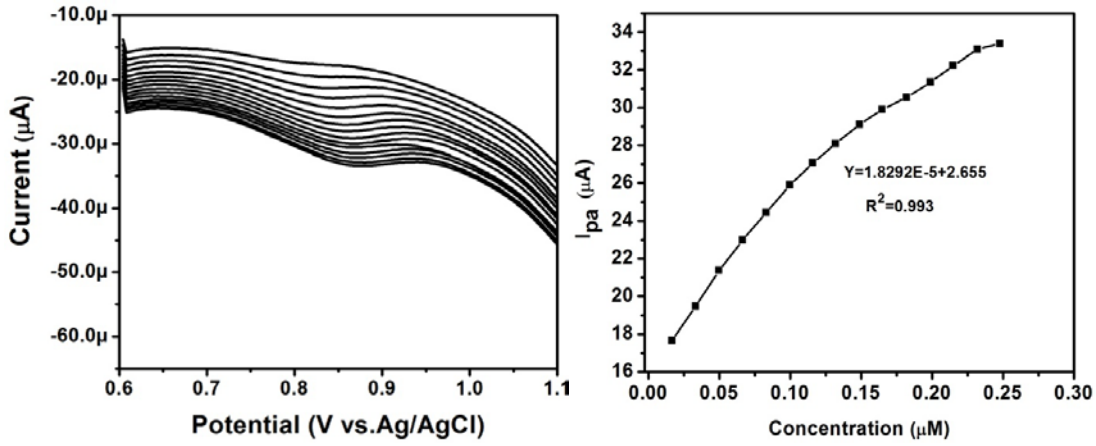


Fig. 7. (a) DPV obtained for poly (CR)/CPE due to the addition of TR in the presence of 0.1 M PBS (pH=7.0); (b) Calibration plot of oxidation peak current *vs* concentration of TR

Table 1. Comparison of detection limit of poly (CR)/CPE with other electrodes for the detection of TR

Modified electrode	**LOD, M**	**Ref.**
SDS/ GCE	6.00×10^{-7}	[30]
ZnO/rGO/CPE	2.0×10^{-9}	[6]
Poly (CR)/CPE	7.3×10^{-6}	This work

Electrochemical work on Terazosin is very limited, in that the literature on SDS/ GCE shows a meagre high sensitivity than our work there the electrode used was GCE, but not CPE. With ZnO/rGO/CPE though the LOD is high but the modifier used is of costlier than the Congo red which is used in our work. In addition the developed method includes real sample analysis gives better results than the other modifiers. This study was sensitive, selective, accurate, precise, cheap and easy to use for the determination of TR in blood serum and injection samples.

3.6. Real sample analysis

Practical performance of the fabricated electrode was validated by the quantitative determination of TR in human blood serum sample (Obtained from the health centre, S.V University, Tirupati, A.P). The procedure followed is as follows: 2 mL of the serum sample without any pre-treatment was diluted to 100 mL with pH 7.0 PBS. Different volumes of this

solution were mixed with a known volume concentration of TR solution and also of known concentration to obtain different concentrations of spiked TR.

Table 2. Determination of TR in the injection samples and human serum (n=3)

Sample	**Sample (mM) Spiked TR**	**Found (mM)**	**Recovery (%)**	**RSD (%)**
Drug Injection	0.1	0.102	102	0.0775
	0.2	0.20	101	0.196
	0.3	0.1	100	0.10
Blood Serum	0.1	0.101	101	0.170
	0.2	0.206	103	0.191
	0.3	0.29	99	0.188

Similarly, a drug injection capsule containing 200 mg of Terazosin HCl suitably diluted in 5 ml distilled water was used to provide the standard concentrations of TR which were analysed by DPV using the poly (CR)/CPE. Each experiment was carried out at least three times and the results were presented in the Table 2. The obtained recovery & relative standard deviation (RSD) were in good, agreement indicating the efficiency of poly (CR)/CPE.

4. CONCLUSION

In the present study we have developed a Poly (CR)/CPE for sensing TR. The Poly (CR)/CPE shows only anodic peak current. The DPV method developed in this study was sensitive, selective, accurate, precise and easy to use for the determination of TR in human plasma. The Poly (CR)/CPE has given some satisfactory results with the detection limit of 7.3×10^{-6} M for TR. Hence, the Poly (CR)/CPE acts as excellent sensor for the determination of TR in the real sample analysis.

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