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Electrochemical Sensor for the Determination of Paracetamol at Carbamazepine Film Coated Carbon Paste Electrode

https://doi.org/10.1515/zpch-2017-0992
Received June 13, 2017; accepted October 24, 2017

Abstract: The electrochemical behavior of paracetamol (PC) was investigated at carbamazepine (CBZ) film coated carbon paste electrode in 0.2 M PBS of pH 7.4 by cyclic voltammetric technique. The modified electrode was exhibited a good electrochemical activity towards the oxidation of paracetamol, which results in a noticeable improvement of the peak currents and feasible oxidation as compared to the bare carbon paste electrode. Under optimal experimental conditions the electrochemical response to PC was linear in the concentration range from 1.0×10^{-4} M to 3.94×10^{-4} M with a detection limit of 0.24 μM by cyclic voltammetric technique. The sensitivity, long-term stability, reproducibility was shown by the modified electrode. Finally, the proposed method was successfully applied to determine PC in pharmaceutical samples.

Keywords: carbamazepine; carbon paste electrode; cyclic voltammetry; electrochemical sensor; paracetamol.

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1 Introduction

The resolution of polymeric organic compound film coated modified electrode sensor is one of the important tool for analysis and quality control of drugs. The development of simple, sensitive, rapid and accurate method for the intensive investigation and determination of drug is of great impact on public health [1].

Paracetamol (PC) (acetaminophen, N-acetyl-p-aminophenol) is generally safe and commonly used dosage as antipyretic analgesics in pharmaceutical formulations [2, 3]. PC is recommended for its fever reliving property; it relieves cough and cold, the pain associated with headache, backache, arthritis, postoperative pain, muscular aches pain, chronic pain and toothache [4–6]. It is also used to treat the patients who are sensitive towards aspirin addiction [7]. PC is rapidly metabolized by undergoing glucuronidation and sulfation to inactive metabolites which are eliminated in urine along with 5% of PC being eliminated unchanged. However, their overdose is toxic in nature and may cause hepatotoxicity and acute liver failure [8]. There are very limited analytical methods are reported for the determination of PC in pharmaceutical formulations such as LC-MS-MS [9], MEKC method [10], gas chromatography-mass spectrometry [11], HPLC GC-MS [12], spectrofluorometry [13], chemiluminescence [14], automatic sequential injection analysis [15], micellar electrokinetic chromatography [16] FT-IR raman spectrometry [17], titrimetry [18], TLC [19] and flow-injection spectrophotometry [20]. However, these reported methods are overpriced, requires tedious extraction procedure, long duration in analysis and complicated. Therefore, it is very important to develop effective analytical method for paracetamol analysis.

Electrochemical sensors and chemically modified electrodes (CMEs) have many advantages in fields like proteomics, biochemistry, molecular biology, nanotechnology, pharmaceutical, food, agricultural and environmental analysis [21–30]. Electroanalytical methods are more preferred because they satisfy many of the requirements such as their inherent specificity, low-cost, fast response, time saving, high sensitivity, good selectivity and simplicity of preparation for the determination of inorganic and organic molecules [31–42].

In the recent years carbon based electrodes especially, carbon paste electrodes and modified carbon paste electrodes have also been incorporated into the electrochemical sensors for determination of biomolecules because of their own unique advantages including low background current, enhanced electronic properties, wide potential windows, low cost, versatility of chemical modification, renewability of the electrode surface and facile kinetics of the electrode processes suitability for detection of various organic and biological compounds. Our research focuses on fabrication of stable working electrode by carbamazepine

film coated carbon paste electrode to achieve feasible electrocatalytic oxidation of PC by cyclic voltammetric technique. Carbamazepine (CBZ) is one of the safest and most effective anticonvulsant drugs. It is a medication used primarily in the treatment of epilepsy, neuralgic pain and bipolar affective disorder. CBZ is a widely used antiepileptic compound and it is metabolized by CYP3A enzyme [43]. CBZ is among the most widely agreed drugs, in pharmaceutical formulations with variety of dosages due to its high catalytic activity, fast and sensitive for biological activity [44]. However, no investigations were reported for the analysis of PC at carbamazepine film coated carbon paste electrode (CBZ/CPE) by cyclic voltammetric techniques. The results indicated that electrochemical responses of PC at modified electrode shows good enhancement when compared to bare carbon paste electrode.

2 Experimental

2.1 Instrumentation

Electrochemical studies were carried out by using an electrochemical work station CHI-660c (CH Instrument-660 electrochemical analyser, USA) coupled with a conventional three-electrode cell. A three-electrode cell was used with saturated calomel electrode (SCE) as a reference, platinum wire as a counter electrode and a self-made bare carbon paste electrode (BCPE) or CBZ/CPE as working electrode. All the potentials were given against SCE.

2.2 Reagents and chemicals

Paracetamol (PC) was obtained from Himedia, (M_{wt} = 151.16 g/mol, purity 99%). Carbamazepine was obtained from sigma Ltd., India (M_{wt} = 236.26 g/mol, purity 99.5%). All chemicals were of analytical grade and used as received without any further purification. All the experiments were carried out at room temperature. The PC stock solution ($C_{PC} = 25 \times 10^{-4}$ M) was prepared by dissolving in double distilled water. Phosphate buffer solution (PBS) of same ionic strength was prepared (0.2 M) by mixing appropriate ratio of $NaH_2PO_4 \cdot H_2O$ and Na_2HPO_4. Graphite powder of average particle size 50 μM purchased from Merck and silicon oil from Himedia was used to prepare carbon paste electrode (CPE). All other reagents used were of analytical grade. All the aqueous solutions were prepared with double distilled water.

2.3 Preparation of bare carbon paste electrode

The BCPE was prepared with the composition of 70:30 (graphite powder:silicone oil) in an agate mortar and grinded for about 45 min until a homogeneous paste was formed. The paste was packed into a homemade cavity of PVC tube of 3 mm internal diameter and the surface was smoothened on a weighing paper. Unless otherwise stated, the paste was carefully removed prior to pressing a new portion into the electrode after every measurement. The electrical contact was provided by a copper wire connected to the end of the tube.

2.4 Preparation of carbamazepine film coated carbon paste electrode

Electrochemical polymerisation of carbamazepine on the surface of BCPE was carried out by using cyclic voltammetric technique. The BCPE was scanned for five multiple cycles in an electrochemical cell containing solution of 1.0 mM carbamazepine monomer in 0.2 M PBS of pH 7.4. The electropolymerisation was achieved by successive cyclic voltammetric sweep between −0.6 V and +1.8 V with the scan rate of 0.1 Vs^{-1}. After that the CBZ/CPE was rinsed thoroughly with double distilled water and used for the determination of PC.

2.5 Determination of PC in formulation tablets

A quantity of five tablets (equivalent to 500 mg of PC in each tablet) of paracetamol were weighed and ground to a homogeneous fine powder in a mortar. A portion equivalent to a stock solution of concentration of about 1.0 mM was accurately weighed and dissolved in doubly distilled water. The contents were sonicated for 10 min to affect widespread dissolution. The excipient was separated by filtration and the residue was washed three times with doubly distilled water. The solution was transferred into a 100 mL calibrated flask and diluted to a final volume with same solvent. Appropriate solutions were prepared by taking suitable aliquots from this stock solution and diluted with 0.2 M PBS of pH 7.4. Each solution was transferred to the voltammetric cell and analysed by standard addition method. The cyclic voltammograms were recorded between 0.0 and 0.8 V with the scan rate of 0.05 Vs^{-1}. To study the accuracy of the proposed method and to check the interferences from excipient used in the dosage form, recovery experiments were carried out. The concentration of PC was calculated using standard addition method.

3 Result and discussion

3.1 Electrochemical polymerisation of carbamazepine on BCPE

The carbamazepine polymer film coated carbon paste electrode was fabricated by cyclic voltammetric technique by multiple potential sweeping the electrode between the potential window of −0.6 V and +1.8 V with scan rate 0.1 Vs^{-1} for five multiple cycles in 0.2 M PBS of pH 7.4 until a stable cyclic voltammogram was obtained as shown in Figure 1. In the oxidation mechanism of the carbamazepine, a radical was formed and covalently linked to the surface of BCPE. This linkage can be controlled by varying the number of multiple cycles. The probable electropolymerisation mechanism of carbamazepine and electrocatalysis interaction with paracetamol is described in Scheme 1. Such types of mechanisms have been proposed in earlier report [45].

The total active surface area available for reaction of species in solution can be estimated by the Randles-Sevcik equation (1) [45, 46]. The cyclic voltammograms were recorded for oxidation of 1 mM potassium ferrocyanide with 1 M KCl as a supporting electrolyte with the different scan rate. For CBZ/CPE the electroactive surface area is maximum (0.0415 cm^2) as compared with BCPE (0.0290 cm^2).

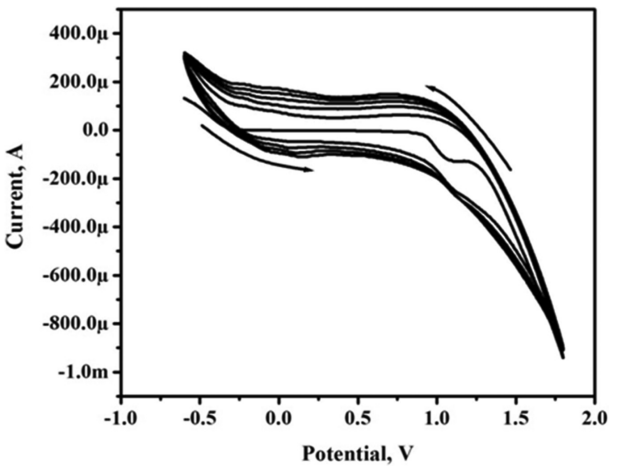
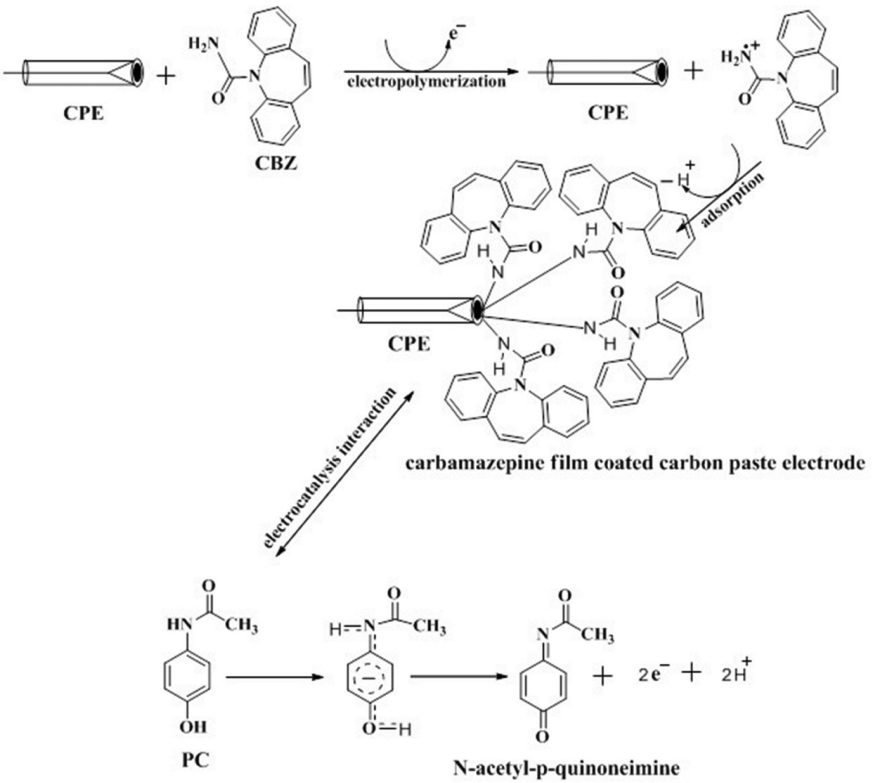


Fig. 1: Cyclic voltammograms of preparation of carbamazepine film coated carbon paste electrode in 1.0 mM solution of carbamazepine in 0.2 M PBS of pH 7.4 at 5 cycles with scan rate of 0.1 Vs^{-1}.



Scheme 1: Mechanism of electropolymerisation of carbamazepine on the surface of BCPE and electrocatalysis interaction of paracetamol with carbamazepine film coated carbon paste electrode.

3.2 Electrochemical response of PC at CBZ/CPE

Firstly, the electrochemical responses of 0.1 mM PC at BCPE and CBZ/CPE in 0.2 M PBS of pH 7.4 with the scan rate 0.05 Vs^{-1} were characterized by cyclic voltammetry as shown in Figure 2. The electrochemical behaviour of PC at BCPE shows a poor voltammetric response due to slow electron transfer phenomenon and the oxidation peak potential occurred at 0.3424 V versus SCE. But, in the same identical condition CBZ/CPE showed great increment in current signals and the oxidation peak potential was observed at 0.3504 V. on the other hand the reversible behaviour of PC was observed at CBZ/CPE. Hence this is a clear evidence of electrocatalytic activity of CBZ/CPE towards the electrochemical oxidation of PC.

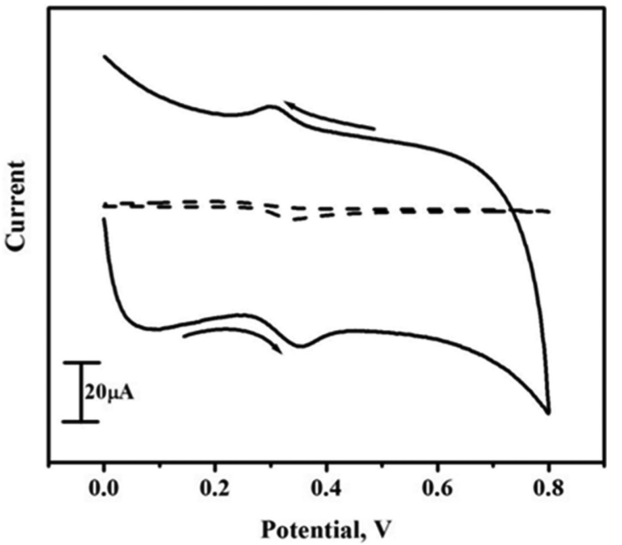


Fig. 2: Cyclic voltammograms for 0.1 mM PC at bare CPE (dashed line) and carbamazepine film coated carbon paste electrode (solid line) in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1}.

3.3 Effect of scan rate on the peak current of PC

The effect of scan rate was studied on the oxidative and reductive peak currents for 0.1 mM PC at CBZ/CPE in 0.2 M PBS of pH 7.4 as a supporting electrolyte by cyclic voltammetric (CV) technique. According to Randles-Sevcik equation the redox peak current is directly proportional to scan rate. The Figure 3A shows the peak current increased with a slight positive shift in the peak potential when the scan rate was increased in the range from 0.025 Vs^{-1} to 0.2 Vs^{-1}. Therefore, The graph of peak current (Ip) versus scan rate (υ) resulted in a straight line with the correlation coefficient (r^2) of 0.9996 and 0.9994 as show in Figure 3B. The Ip versus square root scan rate ($\upsilon^{1/2}$) was plotted as shown in Figure 3C with the correlation coefficient (r^2) of 0.9914 and 0.9911. This suggests that the process of the electrode reaction is controlled by adsorption phenomenon [45–47].

3.4 Effect of pH value on the determination of PC

The effect of pH on the electrochemical oxidation behaviour of PC at CBZ/CPE was carefully studied by CV technique. The Figure 4A illustrates the peak current response of 0.2 mM PC at CBZ/CPE in the pH range of 5.5–8.0. The result shows, by increasing the pH of 0.2 mM phosphate buffer the oxidation potential was shifted

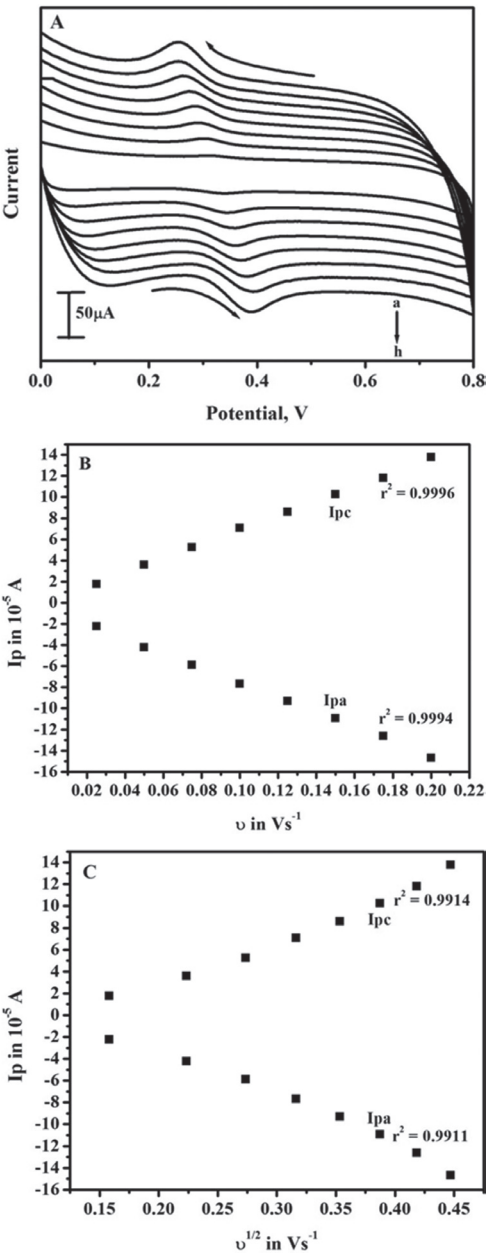


Fig. 3: Effect of scan rate on peak current of PC. (A) Cyclic voltammograms for 0.1 mM PC at carbamazepine film coated carbon paste electrode in 0.2 M PBS of pH 7.4 at different scan rate (a–h; 0.025 Vs^{-1}, 0.05 Vs^{-1}, 0.075 Vs^{-1}, 0.1 Vs^{-1}, 0.125 Vs^{-1}, 0.15 Vs^{-1}, 0.175 Vs^{-1} and 0.2 Vs^{-1}). (B) Graph of peak current (Ip) versus scan rate (υ). (C) Graph of peak current (Ip) versus square root of scan rate ($\upsilon^{1/2}$).

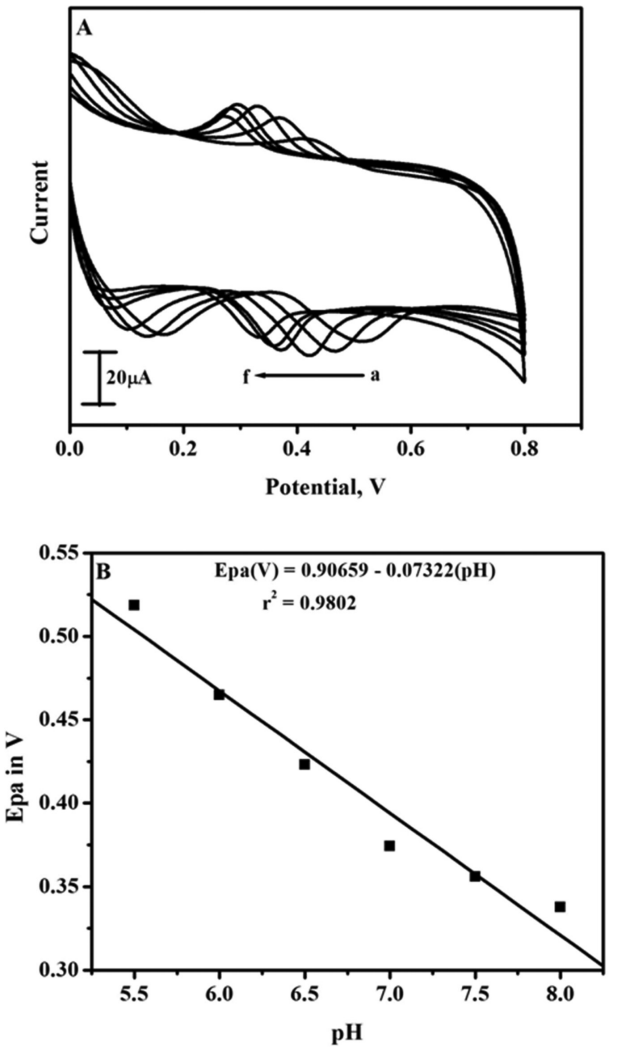


Fig. 4: Effect of pH value on the determination of PC. (A) Cyclic voltammograms obtained for the oxidation of PC at carbamazepine film coated carbon paste electrode in 0.2 M PBS solution at different pH values (a–f: 5.5 to 8.0) at scan rate of 0.05 Vs^{-1}. (B) The effect of pH on the peak potential of PC in 0.2 M PBS solution.

to more negative side. The anodic peak potential (Epa) vs. pH graph clearly indicates that the catalytic oxidation potential depends linearly on the pH with slope of 0.0732 V/pH ($r^2 = 0.9802$) as shown in Figure 4B and signifying that there are an equal number of protons and electrons involved. Our experimental results were in agreement with the literature reports [48, 49].

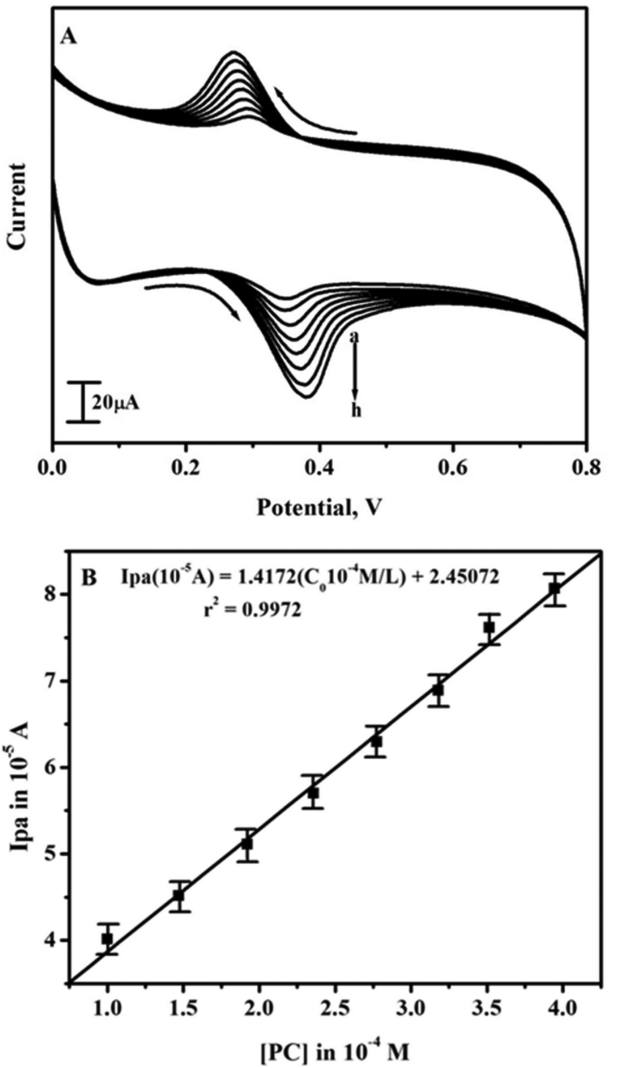


Fig. 5: Effect of PC concentration. (A) Cyclic voltammograms of PC in 0.2 M PBS solution of pH 7.4 at carbamazepine film coated carbon paste electrode at scan rate of 0.05 Vs^{-1} with different concentrations (a–h: 1.0×10^{-4} M, 1.47×10^{-4} M, 1.92×10^{-4} M, 2.35×10^{-4} M, 2.77×10^{-4} M, 3.18×10^{-4} M, 3.51×10^{-4} M, 3.94×10^{-4} M). (B) Graph of anodic peak current versus concentration of PC.

3.5 Effect of PC concentration

In order to develop a voltammetric method for the determination of paracetamol, The electrocatalytic oxidation of PC was carried out by varying its concentration

Tab. 1: Comparison of linear range and detection limits for PC with different classical methods and electrodes.

Classical methods	Electrode/modifier biosensors	Linear working range (μM)	Detection limits (M)	Refs.
ATSDPV	ETPGE	0.05–2.5	2.5×10^{-3}	[50]
AdSSWV	D50wx2/GNP/GCPE	0.0334–42	4.7×10^{-3}	[51]
DPV	N-(3,4-dihydroxyphenethyl)-3,5-dinitrobenzamide – MWCNT/CPE	15–270	1.0×10^{-5}	[52]
CV	C_{60}/GCE	50–1500	0.5×10^{-5}	[53]
Multi-commutated flow system	Nafion-modified glassy carbon tubular electrode	50–500	1.7×10^{-5}	[54]
CV	GCE/Cu complex	20–5000	0.5×10^{-5}	[55]
CV	Carbamazepine film coated carbon paste electrode	100–394	0.24×10^{-6}	Present work

ETPGE: the electrochemically treated pencil graphite electrode. ATSDPV: adsorptive transfer stripping differential pulse voltammetry. D50wx2/GNP/GCPE: a cation exchanger resin, Dowex 50wx2 and gold nanoparticles modified glassy carbon paste electrode. AdSSWV: adsorptive stripping square wave voltammetry. GCE: glassy carbon electrode.

at CBZ/CPE in the range of 1.0×10^{-4} M to 3.94×10^{-4} M in 0.2 M PBS of pH 7.4 at scan rate 0.05 Vs^{-1} as showed in Figure 5A. By increasing the concentration of paracetamol Ipa goes on increasing with shifting Epa towards less positive side. The graph of Ipa versus concentration of PC justifies the reason of increase in anodic peak current and which is due to increase in the concentration of PC as shown in Figure 5B. The graph showed almost straight line with good linearity with the linear regression equation Ipa (10^{-5} A) = 1.4172(C_o 10^{-4} M/L) + 2.4507, (r^2 = 0.9972). The LOD were calculated using the equation, LOD = 3S/M. Where, S is the standard deviation of the peak currents and M is the slope of the calibration curve. The calculated detection limit of paracetamol at CBZ/CPE was found to be 0.24 μM. The detection limit reported for different classical methods and electrodes are tabulated in Table 1. The modified electrode showed the better detection limit as compared to previous reported literatures. The classical method adopted and the limit of detection of analyte obtained was tabulated in Table 1. This method was better compared to other reported literatures [50–55].

3.6 Detection of PC in tablets

In order to evaluate the ability of carbamazepine film coated carbon paste electrode to commercial pharmaceutical samples (500 mg paracetamol per tablet), the CBZ/CPE sensor was applied to determine PC in tablets according to the

Tab. 2: Determination of PC in commercial pharmaceutical sample.

Formulation sample	PC added	Detected[a]	Recovery (%)	SD ± RSD (%)
Tablet (Calpol)	–	Not detected	–	–
	3.0×10^{-6}	3.105×10^{-6}	103.5	0.0741 ± 0.0530
	5.0×10^{-6}	4.970×10^{-6}	99.4	0.0212 ± 0.0151
	7.0×10^{-6}	7.116×10^{-6}	101.6	0.0819 ± 0.0585
	9.0×10^{-6}	9.044×10^{-6}	100.4	0.0311 ± 0.0222
	2.0×10^{-5}	1.901×10^{-5}	95.0	0.0700 ± 0.0500
	4.0×10^{-5}	4.102×10^{-5}	102.5	0.0721 ± 0.0515

[a]Average of five determination.

recommended method. The procedure for the tablet analysis was followed as described in the Section 2.5. The recovery of the CV method was also studied to evaluate the accuracy of the method. The recovery test of PC ranging from 3.0×10^{-6} M to 4.0×10^{-5} M was performed using cyclic voltammetry. As can be seen in Table 2, good recoveries and SD ± RSD were found revealing that the recommended method has good analytical applicability in the determination of PC in pharmaceutical samples. The obtained result indicating that the carbamazepine film coated carbon paste electrode can be successfully used for the selective determination of paracetamol in pharmaceutical samples.

4 Conclusion

In the present work a novel modified carbon paste electrode i.e. carbamazepine film coated carbon paste electrode was developed for the electro oxidation of PC in PBS of pH 7.4 by CV technique. The oxidation peak current signifying that carbamazepine film coated carbon paste electrode exhibits noticeable enhancement effect to the determination of PC as well as under optimal conditions the cyclic voltammetry response to PC has a linear concentration over the range from 1.0×10^{-4} M to 3.94×10^{-4} M, with limit of detection 0.24 μM respectively. The sensitivity, long-term stability, reproducibility was shown by the modified electrode. Overall, a simple modification procedure was reported for the determination of PC by CV technique.

Acknowledgments: We wish to express our gratitude to the Department of Science and Technology and Science and Engineering Research Board, Ref. no:-SERB/F/1217/2014-15 Dated 28-05-2014, New-Delhi for financial support of this work.

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