Novel layered structured bentonite clay-based electrodes for electrochemical sensor applications

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ABSTRACT

The electro-oxidation of cetirizine was studied by employing a chemically changed carbon paste electrode with layered structured bentonite clay. The approach includes identification and its analytical utilizations using voltammetric techniques namely Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV) techniques. The surface morphology of electrode was studied by SEM and AFM analyses. The detection and quantification values obtained were lower and agreeable compared to earlier reported values. The revised electrode showed excellent stability, sensitivity, and improvement of great reproducibility in peak current. The heterogeneous rate constant was also calculated on the basis of the parameters analyzed and their successful effects. The suggested sensor may be applied to the human urine and pharmaceutical samples for drug detection. The suggested methodology was successfully tested for analytical applications with better recovery values.

1. Introduction

The accumulated natural chemical histamine in our body triggers cold or allergy symptoms like sneezing, itching, runny nose, or watery eyes. These symptoms can be prevented by utilizing antihistamine drugs, which usually precludes the amount of histamine in our body, thus relieves from allergic conditions. The Cetirizine (CTZ) is well known non-steroidal anti-inflammatory drugs (NSAIDs) belonging to second-generation antihistamine drug of piperazine class, which inhibits peripheral histamine H_1 receptor [1–4]. Hence, it can be effectively used to cure seasonal allergic rhinitis and chronic urticaria. The CTZ is (Scheme 1) chemically termed as 2-[2-[4[(4-chlorophenyl)-phenylmethyl]piperazin-1-yl]ethoxy]acetic acid [5]. The CTZ is currently sold under trade names Cetiriz, Cetrizet, Cetzine, Zyncet, and Zyrtec in India.

Till today many methods such as spectrophotometry [6,7], chromatography [8–10], etc. have been generated to analyze biomolecules from its pure dosage form or its biological samples. These methods require more duration for analysis, preparation of samples was tedious, high cost, and expert handling. These disadvantages can be overcome by employing electrochemical methods, which include conductometry, potentiometry, amperometry, voltammetry, etc. as these methods provide satisfactory results with low detection limits, less expensive, less time for sample preparation, flexibility and feasibility [11–14].

In the present scenario, the development of electrochemical sensing devices attracts much interest and exploring broader applications in the area of environmental monitoring, food industry, and clinical process [15–18]. The numerous chemically modified electrodes (CMEs) were employed in electrochemical investigations. These sensors explore distinct features such as inertness, the more significant activity of the surface, less fouling effect, reproducibility, reliability with an easy renewal of the electrode surface [19,20]. Carbon-based sensors and metal-based sensors have been extensively used to identify bioactive analyte molecules [21–24]. Enrichment of a working sensor can be achieved by incorporating or loading sensing base with modifiers. Different types of modifiers such as carbon and metal-based nanoparticles, inorganic complexes, clay particles, conducting polymers, ionic surfactants, etc. can be exploited for the surface enrichment of the working electrode. Carbon paste electrodes as a working sensor attracted much attention. It was a most promising sensor, as their preparation was simple, cheap, it provides lower background current with a wide range of potential window, mainly simple to alter. Hence, we used carbon paste to develop electrode to detect analyte molecules [25].
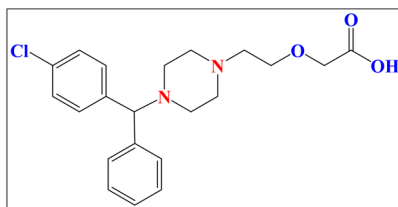
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Scheme 1. Chemical structure of CTZ.

Clay particles are inorganic structural materials and are utilized for the various applications due to their crucial functioning features such as small size, swelling ability with porous nature, ease, and possibly controllable structure compared with the other sensor materials [26–28]. The naturally occurring Bentonite clay (BC) is swelling clay with a porous hydrous aluminosilicate structure having attached silicates and aluminum hydroxide (Si_2O_5 and $Al_2(OH)_4$) forms nano-scaled structure layers. The BC particles are associated with matter, water, and salt and may be regarded as a clay phase, i.e., clay-saltwater gives a single-phase system. The large surface area of BC enhanced the catalytic properties, cation exchangeability with higher thermal and chemical stability [29–35]. Due to the unique qualities of layered structured BC, it was utilized for sensor preparation to get better features.

The documented reports reveal that the detection and analysis of CTZ employed many analytical methods which include spectrophotometry [36,37], potentiometry [38], gas chromatography [39], high liquid performance chromatography (HPLC) [40]. The BC modified electrodes were extensively used in voltammetric measurements to monitor metals in water, bioactive compounds [41,42]. Due to its vast usage and to check its applicability in present work, we utilized a layered structured bentonite clay electrode to detect the target molecule. The electrooxidation of CTZ has not been studied by utilizing layered structured bentonite clay modified electrode (Bent/CPE). The current study focuses on the development of a simple-sensitive sensor based on layered structured BC for the detection and to explore the behavior of CTZ by employing CV and DPV techniques. Real sample analysis was carried out to detect CTZ efficiently by employing a revised sensor.

2. Experimental

2.1. Reagents and chemicals

Unadultred CTZ, Layered structured bentonite clay, were procured from Sigma-Aldrich and employed without any further processing. The stock solution of CTZ with 1.0 mM was produced in doubly demineralized water and preserved at the cold place until further use. The (0.2 M) phosphate buffer solution (PBS) was composed ranging from pH 3.0 to pH 11.2 by dissolving appropriate amounts of H_3PO_4, KH_2PO_4, Na_2HPO_4, Na_3PO_4 in double purified water as per early reports [43]. The rest of the chemicals and reagents utilized were of analytical grade and also entire investigation was maintained by double-distilled water.

2.2. Instrumentation

The potentiostat of CHI Company (D630, USA), was used for recording the electroanalytical measurements. It was connected to the three electrodes, the main operating sensor was a BC carbon paste electrode (Bent/CPE), a platinum string used as an auxiliary (counter) sensor and for a reference sensor, saturated Ag/AgCl (3.0 M KCl) was employed. The pH of the PBS was registered employing pH meter (Elico Ltd., India). All the investigations were performed with an analyte in pH solutions (electrolyte) utilizing a glass cell (10 ml) and an ambient temperature of 25 ± 0.1 ^{0}C was maintained at the entire investigation.

2.3. Pharmaceutical and biological fluids sample preparation

From the local pharmacy, CTZ tablets were purchased and finely powder was made by squashing ten pills. The stock solution was produced with double-distilled water by dissolving prepared powder corresponding to the stock solution of CTZ (1.0 mM). It was taken in a 100 ml calibrated flask and made the volume up to the mark using double distilled water. It was sonicated for ten minutes to achieve complete dissolution. The suitable aliquots of supernatant clear liquid (0.1 ml, 0.2 ml, etc.) were added to 0.2 M phosphate buffer solution (PBS) of pH 6.0 (produced by dissolving 1.84 g of KH_2PO_4 and 0.305 g of Na_2HPO_4 in 200 ml double purified water) to prepare appropriate solutions. Each solution was then transferred to a 10 ml voltammetric compartment (0.1 ml of sample solution + 9.9 ml of buffer, 0.2 ml of sample solution + 9.8 ml of buffer, etc.) and analyzed by the standard addition method. The detection, along with recoveries of CTZ, was studied by employing the DPV technique, and voltammograms were registered within 0.2 – 1.6 V after accumulation for 90 s with stirring. The anodic oxidation peak for CTZ was measured. Further, the amount of CTZ was calculated utilizing the standard addition method (A known quantity of standard solution in different concentrations was added to several solutions containing the same amount of unknown solution).

The human biological samples like urine samples were taken from healthy volunteers, and for 5 min at ambient temperature (25 ± 0.1 ^{0}C), it was centrifuged. Then the samples were diluted twice by employing a PBS solution of pH 6.0. Then the known amount of CTZ (1.0 mM) was added to this sample of human urine to produce biological test solutions.

2.4. Construction of modified electrode

The revived electrode Bent/CPE, was arranged by merging, graphite powder (7.0 g) with an appropriate amount of bentonite clay (0.05 g) and firmly homogenized. Later a few drops of liquid paraffin oil (3.0 ml) were mixed to get modified carbon paste. After complete homogenization, it was loaded inside the vacant region of polytetrafluoroethylene (PTFE) tube affixed to copper wire for exterior connection and polished against filter paper. Finally, it was carefully cleaned employing doubly-purified water to remove the impurities that adhere to the PTFE tube. The sensing vicinity of electrode was activated by measuring the cyclic voltammograms in a 6.0 pH solution with a potential range of 0.2 – 1.6 V at a 50 mVs^{-1} scan rate for 20 cycles. Then, this activated sensor compartment was fixed in a container comprising of 1.0 mM CTZ. The excellent reproducibility of the electrode was earned by restoring the surface of the electrode by fresh paste. Correspondingly, pure CPE was produced in the same method without adding BC. Carbon paste electrode has a wide range of working potential

3. Results and discussions

3.1. Active surface of sensor

The key functioning space of the sensor is an active surface area of the sensor. In this present examination, the functioning electrode surface was determined by inheriting the Randles-Sevcik equation (1). Different sweep rates measured at 25 ^{0}C utilizing 0.1 M KCl solution and 1.0 mM $K_3[Fe(CN)_6]$ by adopting CV techniques [44]. We calculated active area of electrode for both pure CPE and revived electrode found to be 0.042 cm^2 and 0.083 cm^2 respectively. The equation (1) was given as below;

$$Ip = (2.69 \times 10^5)n^{3/2}A\ D_0^{1/2}\upsilon^{1/2}C_0* \tag{1}$$

Here, 'n' is the quantity of electrons participated in the reaction mechanism, i.e., equal to 1, whereas A is the active surface area of the electrode base, 'D_0' is diffusion coefficient and its value is 7.6×10^{-6}
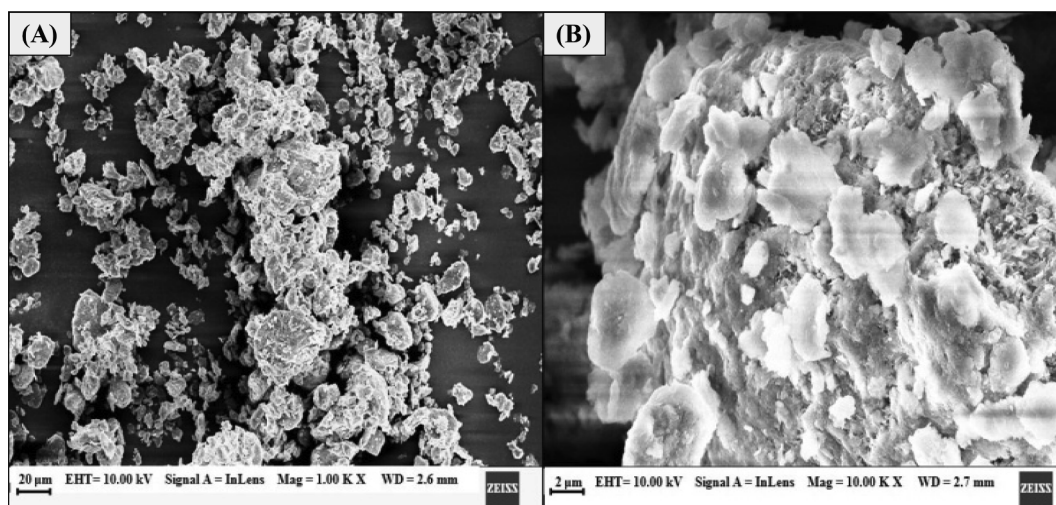
Fig. 1. Surface morphology features of bentonite clay particles: (A) and (B) SEM images.

$cm^2 s^{-1}$, 'υ' is scan rate and 'C_0*' is the concentration of $K_3[Fe(CN)_6]$ solution.

The morphological study of the modified electrode was investigated by SEM (Fig. 1) and AFM analyses. Fig. 1A and 1B represent the low and high magnification images of layered clay particles achieved by scanning electron microscope. In both images, a "cornflake" like a layer of bentonite clay sheets was observed. This layered structure particle assembly provides a greater surface area and helpful for adhering more number of CTZ molecules.

Fig. 2 represents AFM images of CPE and Bent/CPE. The roughness of the electrode surface and delta Z value was obtained from AFM topological images. These images indicate that total roughness was increased in Bent/CPE (Fig. 2B) than CPE (Fig. 2A) indicates that the effective modification of carbon paste with BC particles. The delta z value for bare and modified electrode was 1.17 nm and 232.1 pm, respectively. The increased surface area of the electrode after modification is contributed to the layered structured BC, and this enhancement of the surface increases the transfer of electron at a faster rate.

3.2. Effect of pre-concentration time

At pre-concentration time (t_{acc}), maximum analyte molecules gather near the vicinity of the sensor. Hence, pre-concentration–time was evaluated by employing a cyclic voltammetric method within a 0 – 120 s time span. A plot of peak current vs. accumulation time (Fig. 3) indicates, 0 to 90 s, peak current values show a progressive expansion,
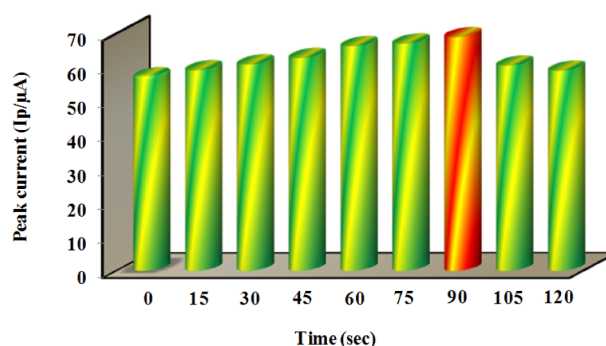

Fig. 3. Effect of variation of accumulation time for 1.0 mM CTZ.

and further peak current were declined with constant values. The maximum enhancement of the peak current was recorded at the 90 s. Hence, arresting 90 s as accumulation time, further criteria were inspected.

3.3. Voltammetric behavior of CTZ

The voltammetric nature of CTZ (1.0 mM) was inspected at pure CPE and Bent/CPE in PBS of pH 6.0 at 50 mVs^{-1} by adopting cyclic voltammetric techniques. The earned voltammograms were visualized in Fig. 4; it was noted that at both the electrodes, there was an anodic
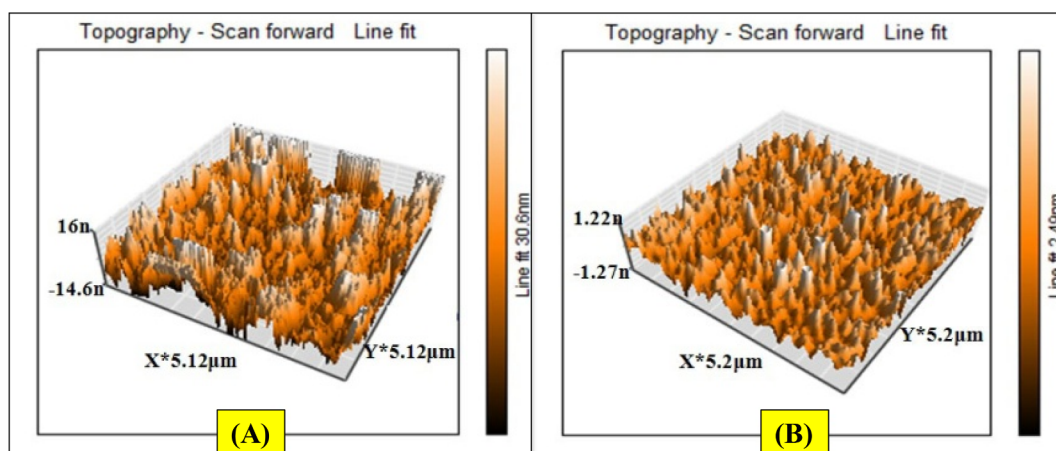

Fig. 2. AFM image of (a) unmodified carbon paste electrode, and (b) bentonite clay modified carbon paste electrode.
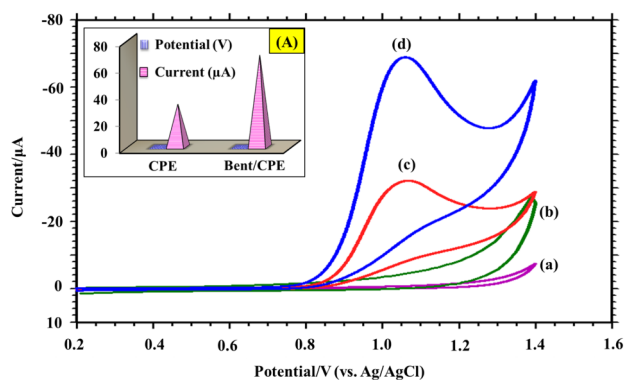
Fig. 4. Voltammetric performance of 1.0 mM CTZ at pH 6.0, PBS (I = 0.2 M) at a scan rate of 50 mVs^{-1}; t$_{acc}$ = 90 s; (a) At bare CPE; (b) At bentonite clay/CPE; (c) At bare CPE (1.0 mM CTZ) ; (d) At bentonite clay/CPE (1.0 m CTZ); (A) difference in peak current and peak potential at two different electrodes.
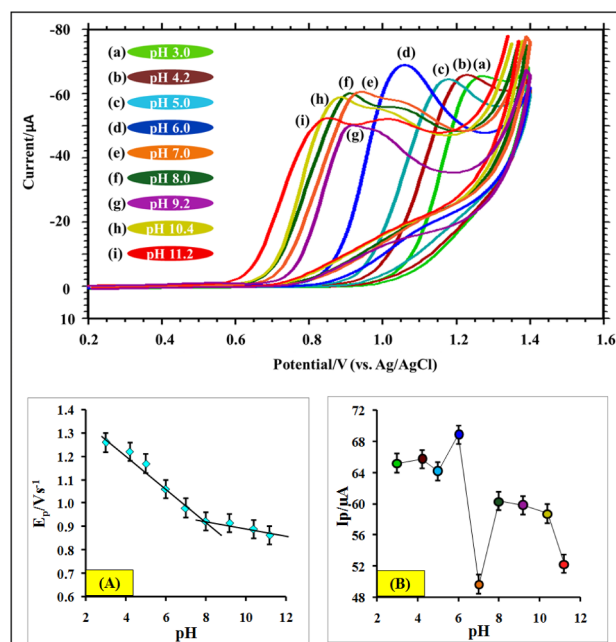

Fig. 5. Cyclic voltammograms achieved for 1.0 mM CTZ in phosphate buffer of variegated pH at Bent / CPE; scanning rate = 50 mVs^{-1}; t$_{acc}$ = 90 s; (A) The pH effect on the peak potential (Ep / V) of CTZ; and (B) impact of different pH on peak current (Ip / μA) of CTZ.

peak with 32.08 μA and 68.88 μA peak current for pure CPE and Bent/CPE, respectively. The intensification of peak current (two fold) including a reduction in potential peak values suggests that the electrode was effectively modified with bentonite clay particles, which expanded the electrode's surface region. Further, the reverse scan indicates the absence of cathodic peaks indicates an irreversible electrode process of CTZ at Bent/CPE. The voltammograms were registered between potential range of + 0.2 to + 1.6. For pure CPE, we got an oxidation peak at + 1.06 V, and at Bent/CPE intensified oxidation peak was registered with potential + 1.05 V (Fig. 4). Hence, +1.05 V (working potential) is selected as an optimal potential for all investigations.

3.4. pH of supporting electrolyte

The pH of the supporting electrolyte immensely influences the activity of the sensor. This effect was studied on the electro-oxidation of CTZ by employing the CV technique with a varied pH range of pH 3.0 – pH 11.2 of PBS (I = 0.2 M) solution. The voltammograms were shown in Fig. 5. The involvement of protons during the electro-oxidation of CTZ was evident due to the shifting of the potentials peak values to lower positive values with increment in the pH of the solution. The obtained voltammograms indicate that as the solution pH was raised, anodic peak current was enhanced up to pH 6.0. Further, a decline in peak current values was noticed at higher pH, and the highest response was documented at pH 6.0 (Fig. 5A); hence, the same was retained to investigate other parameters.

The bentonite clay surface exhibits a point of zero charge (pzc) in the lower pH limits (3.0 – 4.2), and the clay surface is positively charged under pzc at lower pH. When pH value is changed (5.0 – 6.0), the value above pzc, the surface of the clay electrode becomes negatively charged [45]. The acidic constant (pKa) of CTZ is 8.0 and CTZ predominates in the ionic form in the pH conditions from 3.0 to 8.0 [46–48]. The ionic form of CTZ facilitates the greater interaction with the negatively charged surface of BC at pH 6.0 (nearer to the acidic constant of CTZ); hence, an increased oxidation peak was obtained at pH 6.0. Later, an increment in the pH may form precipitation; hence, lower anodic peak current values were noticed.

The graph of pH vs. peak potential is displayed in Fig. 3B. Thus, two slopes were obtained. The first slope lies in between pH 3.0 and pH 8.0, showing a slope of 70 mV/pH. Whereas, the second slope was observed between pH 8.0 - pH 11.2 with a slope value of 56 mV/pH. The obtained slope values signifying that an equivalent quantity of protons and electrons take part at the electrode process [49]. The linear regression equation is as follows; Ep = -0.070 pH + 1.50; R^2 = 0.975 (between pH 3.0 – pH 8.0) and Ep = -0.067 pH + 0.98; R^2 = 0.941.

3.5. Study of sweep rate variation

The sweep segments variation study helps to interpret the physicochemical parameters. We obtained cyclic voltammograms (Fig. 6) in PBS of 6.0 pH by fluctuating sweep segments from 10 to 250 mVs^{-1} at Bent/CPE. The anodic peak of CTZ was more intensive as an upswing in sweep rates. The linear dependence of Ip and υ$^{1/2}$ was earned (Fig. 6A) along with a linear regression equation; Ip = 374.42 υ$^{1/2}$ – 8.2119; R^2 = 0.9788.

When we constructed a plot of log Ip vs. log υ, a linear regression equation for this plot was earned and given as; log Ip = 0.4818 log υ + 2.5163; R^2 = 0.9679 (Fig. 6B). The slope value of 0.4818 was nearer to the theoretical value of 0.5, proved that an electrode process was diffusion-controlled mechanism at the Bent/CPE [50].

The observations were made on a graph of Ep vs. log υ (Fig. 6C) linear relation was noted and earned linear regression equation as follows; Ep = 0.0512 log υ + 1.1098; R^2 = 0.9414.

Inheriting the Laviron equation for irreversible electrode process relation between scan rate (υ) and peak potentials (Ep) was studied [51].

$$Ep = E^0 + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right)\log \upsilon \tag{2}$$

Here, 'α' is the transfer coefficient, 'k^0' is the heterogeneous rate constant of the reaction, the number of electrons transferred is denoted by 'n', sweep rate as 'υ', and formal redox potential as E^0. Bard and Faulkner's equation was adapted to calculate 'α' value [52].

$$\Delta E_p = E_p - E_{p/2} = \frac{47.7}{\alpha n}m\upsilon \tag{3}$$

Here, E$_{p/2}$ is the potential where the current is at the half peak value. To calculate the number of protons in irreversible reaction the formula is given as;

$$\delta Ep/\delta pH = 0.059X/\alpha n \tag{4}$$

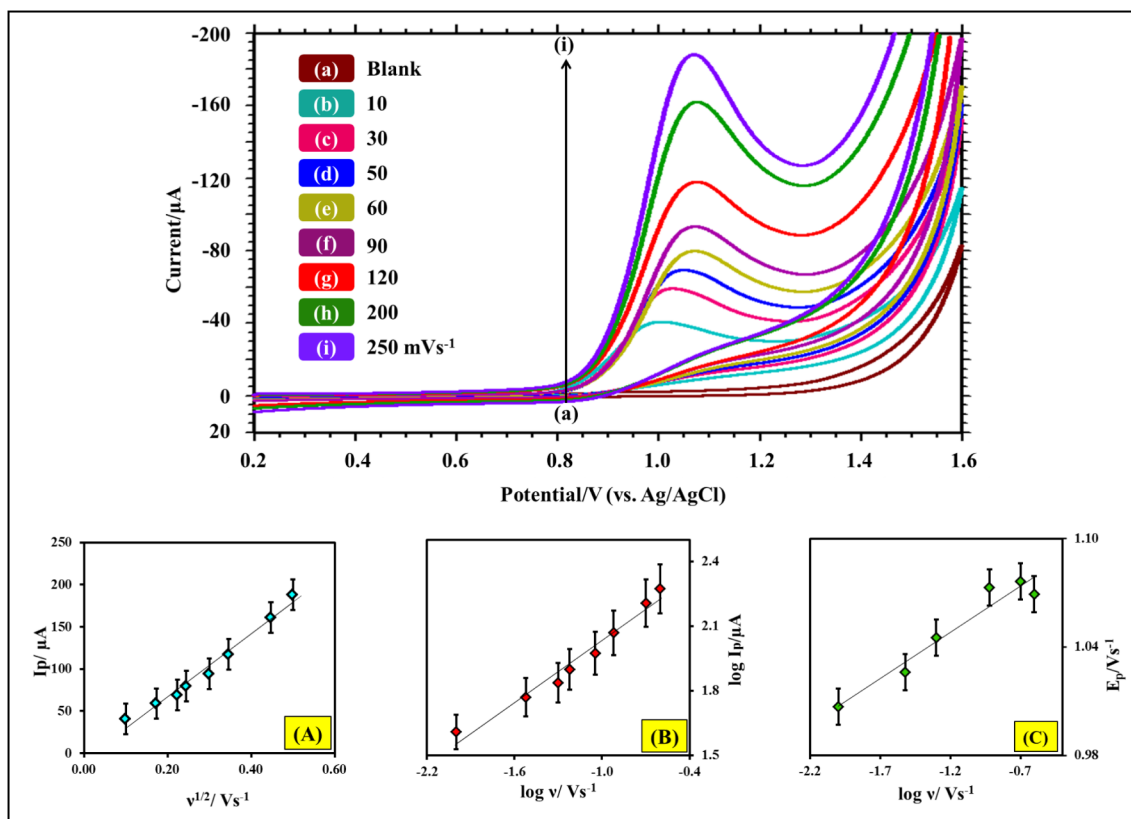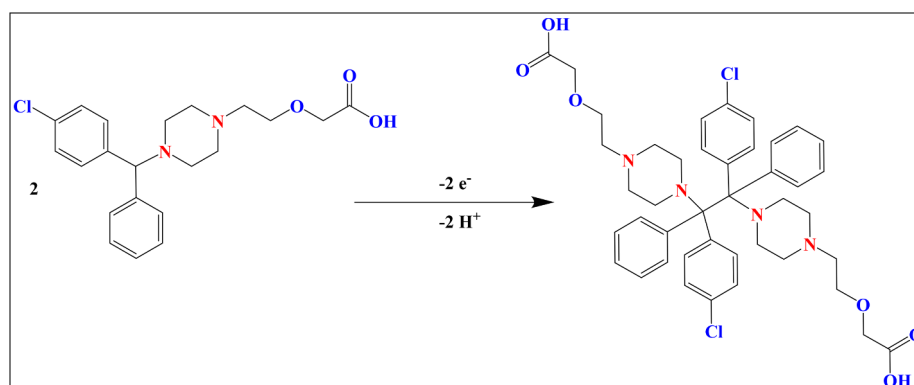Where, X is the number of protons involved during the reaction. The

Fig. 6. Cyclic voltammograms for 1.0 mM CTZ in pH 6.0 PBS with different scan rates at Bent/CPE; pH = 6.0; t_{acc} = 90 s; (A) Effect of variation of scan rate (υ / Vs^{-1}) on the peak current (Ip / μA) of CTZ; (B) Influence of log scan rate (log υ / Vs^{-1}) on the log peak current (log Ip / μA) of CTZ; and (C) Influence of log scan rate (log υ / Vs^{-1}) on the peak potential (Ep / V) of CTZ.

computed 'X' value is 2, 'α' value was found to be 0.56, k^0 was 3.83×10^3 s^{-1}, and 'n' was 2. Hence, two protons and electrons were transferred at the electro-oxidation process.

3.6. Probable electrode mechanism of CTZ

A well-resolved oxidation peak was obtained in the pH range of 3.0 – 11.2, but the maximum peak was observed at pH 6.0. The total number of electrons and protons engaged during the process was counted as two (1 electron and proton from each slope). Therefore, based on the examined parameters, the CTZ electro-oxidation mechanism involves two protons and electrons. CTZ electro-oxidation mechanism is presented in Scheme 2.

4. Analytical characteristics

4.1. Variegated concentration and detection limit

The revised sensor applications were explored at variegated concentrated solution of CTZ in appropriate pH 6.0 PBS by exploiting the DPV technique with working potential of (vs. ref. electrode) + 1.05 V. The low concentration of CTZ can be efficiently detected by DPV, as it provides sharper and well-defined peaks. The augmented peaks were detected as a result of an increase in the CTZ concentration. The achieved differential pulse voltammograms were shown in Fig. 7. The calibration curves were achieved by constructing a plot of peak current (Ip) vs. concentration (C) of CTZ (Fig. 7A) and earned linear regression equation given as follows; Ip = 27.78C + 0.383; R^2 = 0.996. Adopting the limit of detection (LOD) and limit of quantification (LOQ)
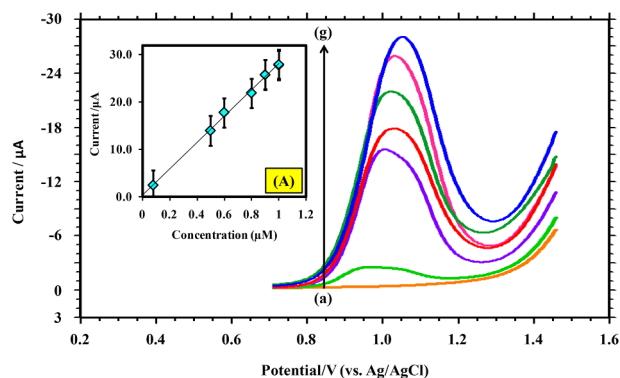

Scheme 2. Probable electro-oxidation mechanism of CTZ.

Fig. 7. Differential pulse voltammograms for increasing CTZ concentrations at Bent / CPE in pH 6.0 PBS; t_{acc} = 90 s; (a) blank, (b) 0.08, (c) 0.5, (d) 0.6, (e) 0.8, (f) 0.9, (g) 1.0 μM; Inset: (A) Effect of variation of concentration (C / μM) on the peak current (Ip / μA) of CTZ.

equations, results were computed as 5.91×10^{-8} M and 19.70×10^{-8} M, respectively. The sensitivity of the method was found to be 2.77×10^{-7} μA μM^{-1} cm^{-2}.

$$LOD = 3S/M \tag{5}$$

$$LOQ = 10S/M \tag{6}$$

In equation (5) and (6) 'S' as the standard deviation of the peak current of blank and 'M' as the slope of the calibration curve. The particulars of the calibration plot are given in Table 1. Further, comparison of developed method with the documented reports, are represented in Table 2.

4.2. Tablet sample analysis

The revised sensor effectiveness was triggered by tablet analysis. The preparation of the tablet sample solution was produced according to section 2.3. Test samples were introduced with appropriate amounts of CTZ and tablets were analyzed for CTZ by adopting the DPV technique. The obtained recovery range is 96.1 – 98.6%, with average values of 1.02% RSD. The results of the method were listed in table 3.

4.3. Interference studies

The revised sensor selectivity and behavior of CTZ in the presence of some common interference was explored by scrutinizing the excipients study, adopting the DPV technique. Fig. 8 displays that the presence of 100 folds of excipients such as ascorbic acid, citric acid, glycine, lactose, starch, tartaric acid, glucose, urea, uric acid and cysteine alter the voltammetry signals for CTZ within threshold limit, i.e., ± 5%. Therefore, the developed sensor is selective for efficient determination of CTZ in existence with excipients.

Table 1
Characteristics of CTZ calibration plot using differential pulse voltammetry at Bent/CPE.

Linearity range (M)	2.0×10^{-9} – 8.0×10^{-4}
Slope of the calibration plot (μA M^{-1})	27.78
Intercept (μA)	0.385
Correlation coefficient (r)	0.996
RSD of slope (%)	0.0022
RSD of intercept (%)	0.0014
Number of data points	6
LOD (M)	5.91×10^{-8}
LOQ (M)	19.70×10^{-8}
Repeatability (% RSD)	0.056
Reproducibility (% RSD)	0.127

Table 2
Comparison of detection limits of CTZ with other methods.

Methods	LOD (M)	References
Glassy carbon electrode	4.3×10^{-6}	[20]
Pretreated pencil graphite electrode	0.2×10^{-6}	[53]
Spectrophotometric determination of cetirizine	2.4×10^{-7}	[54]
Bentonite clay modified carbon paste electrode	5.91×10^{-8}	[Present work]

Table 3
Application of DPV technique for the determination of CTZ in tablet samples at Bent/CPE and recovery test.

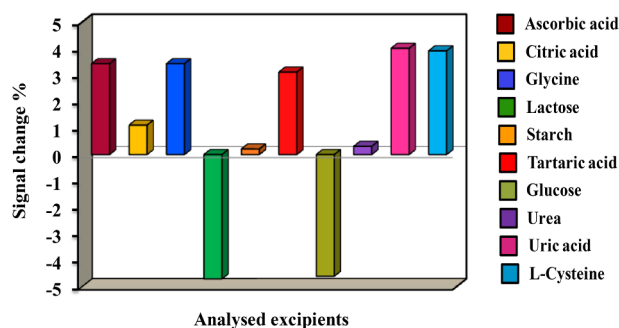| Labelled claim (mg)	100
Amount found (mg)*	98.05
RSD (%)	1.10
Added (mg)	1.00
Found (mg)*	0.9736
Recovered (%)	97.36
RSD (%)	1.02

* Average of five determination.

Fig. 8. Effect of excipients on CTZ's electro-oxidation behavior.

4.4. Spiked human urine sample analysis

The revised sensor's reliability and dependability were validated by real sample analysis. Sample preparation was performed, as mentioned in section 2.3. A known quantity of CTZ was spiked into drug-free samples of human urine, and the amount of CTZ was detected by adopting a sensitive DPV method. The unknown amount of analyte was determined by standard plots, and recovery measurement was done. We earned 96.9 – 97.6% recovery results with 1.2% RSD. Good values of recovery indicate the utility and relevancy of the developed method for the successful identification of CTZ from biological samples. The results were listed in table 4.

4.5. Repeatability and reproducibility of the sensor

The repeatability of the revised sensor was checked by repeated detection of 1.0 mM CTZ at Bent/CPE. The detection of CTZ (five measurements) with regular intervals within day gives RSD of peak current 2.82%. The repeatability of the electrode between days is the

Table 4
Application of DPV technique for the determination of CTZ in spiked human urine samples at Bent/CPE.

Urine samples	Spiked (10^{-4} M)	Detected* (10^{-4} M)	Recovery %	RSD	RSD %
Sample 1	0.1	0.0976	97.60	0.0120	1.209
Sample 2	0.3	0.2873	95.76	0.0123	1.23
Sample 3	0.5	0.4845	96.90	0.0121	1.21

* Average of five determination.

same as within-day with a constant temperature.

The reproducibility of the modified sensor was checked (fresh paste was filled after each measurement) with regular intervals within one day by placing the modified sensor in a cell consisting of PBS (pH 6.0) and CTZ (1.0 mM) solution at a steady temperature. The recorded peak current shows 2.5% of RSD value; it suggests that the modified sensor exhibits good reproducibility towards the detection of CTZ. Further, the oxidative species adhere to the sensor's exterior surface; hence, continuous voltammetric measurements give diminished peak current signals; therefore, after every measurement electrode has to be refilled to yield better results.

The steadiness of the revised sensor was investigated by securing the sensor about 20 days in an airtight jar. The earned results specify that the actual peak current response for 1.0 mM of CTZ was conserved by the revised sensor in the range of 96.2 – 97.8%, suggesting, the steadiness of the sensor.

5. Conclusions

A simple, sensitive bentonite clay embedded carbon paste electrode was generated to determine the CTZ. The morphological features of electrode materials studied by SEM and AFM analyses. The nature of CTZ was explored on both bare/CPE and bentonite clay/CPE by employing CV, and DPV techniques with rising in the peak current were documented due to the usage of bentonite clay particles. Higher responses were registered with pH 6.0 media. The electrooxidation nature of CTZ was irreversible with a diffusion-controlled mechanism involving two-electron and proton. The lowest detection limit (5.9×10^{-8} M) was observed, indicating the sensitivity of the revised sensor. Further, CTZ was accurately detected from biological and pharmaceutical samples by employing the revised sensor. The developed strategy is accurate, sensitive, selective, and precise to detect the CTZ.

CRediT authorship contribution statement

Pramod R. Vernekar: Investigation, Writing - original draft. **Nagaraj P. Shetti:** Resources, Writing - review & editing. **Mahesh M. Shanbhag:** Formal analysis. **Shweta J. Malode:** Writing - review & editing. **Ramesh S. Malladi:** Visualization. **Kakarla Raghava Reddy:** Conceptualization, Writing - review & editing

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2020.105441.

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