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Novel Zeolite Modified Carbon Paste Electrode for Differential Pulse Voltammetric Assay of Cyclopentolate hydrochloride

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Cyclopentolate (CLO) is an antimuscarinic compound with actions similar to atropine which induces both mydriasis and paralysis of the ciliary muscle. The present work describes the fabrication of novel carbon paste electrodes (CPE) incorporated with zeolite as a promising analytical protocol for sensitive voltammetric assay of cyclopentolate. Remarkable enhancement of the sensitivity towards CLO was achieved compared with the blank electrode. An irreversible oxidation process with the two-electron transfer was reported elucidated with molecular orbital calculations. The recorded peak currents were linearly proportional to the CLO within the concentration range 48.03 to 725.00 ng mL^{-1} with LOD of 14.53 ng mL^{-1}. High sensitivity, fabrication reproducibility, and stability were achieved. Noticeable resolution between the cyclopentolate and phenylephrine voltammetric peaks offers simultaneous assay of cyclopentolate in different pharmaceutical formulations in presence of phenylephrine, excipients, or CLO degradation products. The achieved sensitivity and selectivity demonstrate the applicability of zeolite based sensor for determination of cyclopentolate with average recoveries agreeable with the official pharmacopeial methods.

Keywords: Cyclopentolate hydrochloride; Differential pulse voltammetry; Carbon paste electrode; Zeolite Y; Molecular orbital calculations.

1. INTRODUCTION

Cyclopentolate (CLO) is an antineoplastic compound with acts close to atropine that causes ciliary muscle paralysis and mydriasis (cycloplegia), resulting in lens accommodation failure. Cyclopentalate was used for diagnosis, therapeutic of synechia in uveitis, and premedication for

intraocular surgery because of its mydriatic effect [1-6]. It can be also used to oppose the muscarinic and central nervous system through blocking of the acetylcholine receptor in the sphincter muscle of the iris and the ciliary muscle, which prevent the contraction and dilates the pupil.

European Pharmacopeia reported the potentiometric titration of CLO against NaOH as standard official method [7]. The most traditional protocols for assaying CLO in biological fluids and medicinal dosage are chromatographic and capillary electrophoretic approaches. For chiral classification of therapeutic enantiomers, capillary electrophoresis based on β-cyclodextrins derivatives was used [8-11]. Chromatographic protocols including chiral liquid chromatography [12-14], thin-layer chromatographic [15-17] and gas chromatography [18] were reported in literature. Moreover, a visible spectrophotometric based on reaction of CLO with Folin-Ciocalteu (FC) forming a greenish blue colored species was developed for the CLO determination in ophthalmic solutions [19]. An extractive spectrophotometric method was introduced via formation of CLO-bromothymol blue or, -methyl orange colored complexes in the chloroform layer [20].

Chromatographic and spectrophotometric methods offer acceptable sensitivity and wide applicability, but the expensive instrumentation requirements, consumption, and exposure to organic solvents with tedious and time-consuming sample preparation obstacles their application for routine analysis of large sample numbers. On the other hand, electroanalytical methods are enabled to screen many electroactive species in the same run with acceptable selectivity and sensitivity. Applications of electroanalytical approaches were reported for the determination of various pharmaceutical species [21-28].

There is no electrochemical method reported in literature for cyclopentolate determination. A novel differential pulse voltammetric (DPV) study protocol for CLO assessment in eye drop samples using carbon paste electrodes with zeolite Y nanostructure is presented here. The current sensors have a simple improvement and regeneration procedure, as well as a high sensitivity and long life.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Synthetic graphite powder (1-2 µm, Aldrich) and paraffin oil (PO, Merk) were used for fabrication of the carbon paste working electrodes. Zeolite Y (sigma-Aldrich, NISTRM8850), copper oxide nanopowder (30-50 nm, Alfa Aesar), zinc oxide nanopowder (<100 nm, Sigma- Aldrich), and iron (III) oxide nanopowder (<50 nm, Sigma- Aldrich) were tested as electrode modifier. The assisting electrolyte was universal buffer, which was modified to the optimal pH value with NaOH.

2.2. Drug substance

Stock CLO solution was freshly prepared by dissolving standard cyclopentolate hydrochloride (2-dimethylamino-ethyl 2-1-hydroxycyclopentyl-2-phenylacetate, $C_{17}H_{26}ClNO_3$, 327.8 g mol^{-1} with a purity of 100.10 ± 1.30) in water.

2.3. Pharmaceutical formulation

Pentolate (cyclopentolate 1% eye drops 10 ml, Amoun, Cairo, Egypt) was purchased from local market. Cyclophrine eye drops (Cyclopentolate 1% and Phenylephrine 10% Kahira, Cairo Egypt) was tested for the simultaneous assay of phenylephrine and CLO. Cyclopentolate was assayed according to the proposed methods and the recoveries were compared with liquid chromatographic analysis protocol using 4-chlorophenol in methanol as internal standard and mobile phase of 0.2M sodium dihydrogen orthophosphate / methanol with spectrophotometric detection at 254 nm.

2.4. Preparation of CLO alkali degradation products.

The alkaline degradation process was performed by dissolving CLO in 1.0×10^{-1} mol L^{-1} NaOH and incubation for 2h at ambient temperature. The pH was adjusted with HCl and completed to the mark with methanol [29].

2.5. Working electrode

The working blank carbon paste electrodes were fabricated through blending of 0.2g graphite powder and 80 µl paraffin oil and packing the resulting paste into the Teflon piston holders [30]. Electrode modification was performed by replacing 7.5% of the carbon powder with Zeolite. Voltammetric measurements were carried out using 797 VA Metrohm voltammetric analyzer (Metrohm, Switzerland) accompanied with platinum as an auxiliary and Ag/AgCl double-junction reference electrodes.

2.6. Measuring procedures

Aliquots of the CLO fresh stock solution were added to the measuring cell containing BR at pH 10.0 followed by recording the differential pulse voltammograms at the following measuring parameters: pulse height 0.050 V, scan rate 0.040 mV s^{-1}, pulse width 100 ms with pulse time 40 ms. The corresponding peak currents were plotted against the CLO concentration in ng mL^{-1} scale range.

2.7. Molecular orbital calculations

To confirm the proposed reaction mechanism, computational molecular orbital calculations were exetended using Gaussian 09 suite programs [31].

3. RESULTS AND DISCUSSION

3.1. Oxidation of cyclopentolate at the electrode surface

There is no reported work describing the electrochemical behavior of cyclopentolate, therefore, its electrochemical features were explored on the blank carbon paste electrodes and those incorporated with different nanomaterials over a wide potential window (Fig.1 a, b). Cyclic voltammograms of cyclopentolate on the blank carbon paste surface showed an anodic peak at 1.09V considering the irreversibility of the CLO oxidation mechanism without documenting cathodic peaks. Incorporation of zeolite Y (ZY) with the electrode matrix resulted in a noticeable improvement of the peak current (about 23 fold) with shifting of the oxidation peak towards the negative direction. This enhancement may be attributed to the modification with ZY of increased surface area and the accumulation of more amounts of analyte on the electrode. Following, the ZY content within the electrode matrix was varied from 2.5 to 10%, and 7.5% was the optimum (Fig.1 b).

Compared with ZY as modifier, carbon paste electrode modified with ZnO, CuO or FeO nanoparticles were tested for CLO voltammetric assay. Zeolite as electrode modifier showed higher peak current (6, 5 and 10 fold) compared with the aforementioned metal oxides in the same order confirming it superiority for CLO determination (Fig. S1).

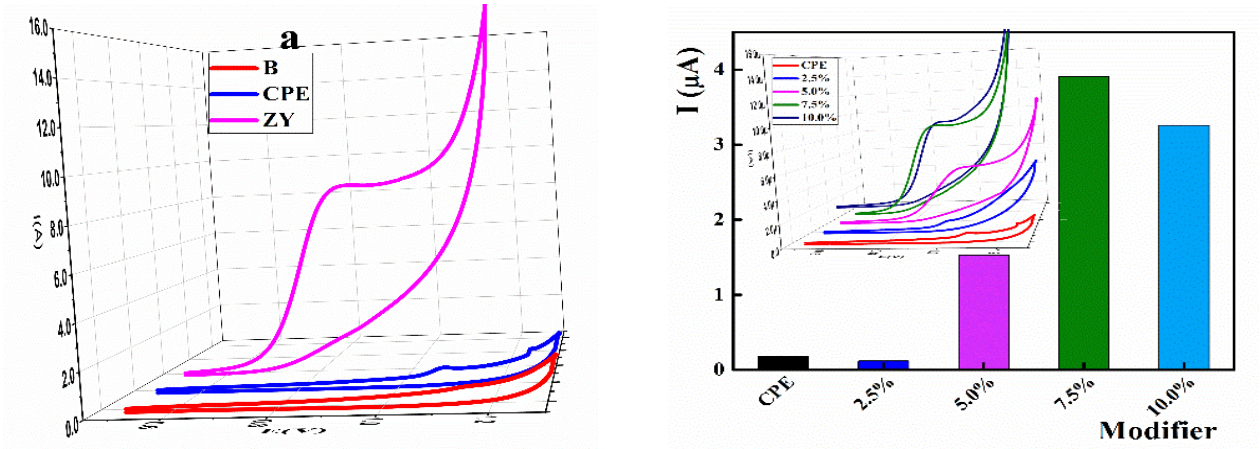


Figure 1. Voltammetric behavior of 275 ng mL^{-1} cyclopentolate on ZY/CPE in BR buffer at pH 10. Scan rate 40 mV s^{-1}.

The electrode surface area was explored by recording the cyclic voltammograms of $K_3Fe(CN)_6/K_4Fe(CN)_6$ at different scan rates. The electroactive surface area of the fabricated sensors was 0.025 and 0.22 cm^2 for the bare and ZY/CPE, respectively, according to the Randles-Sevik equation [32]. On the blank carbon paste, the successive voltammograms showed a noticeable diminishing of the DPV peak with shifting of the peak potential to the positive direction (Fig. S2), which may be attributed to the adsorption of CLO and/or its oxidation products on the electrode surface [26, 33]. Noticeable enhancement was achieved via modification with zeolite nanostructure. One of the most promising futures of the carbon paste electrodes over other solid working carbon

electrodes, including glassy carbon and graphite electrodes, is the ease of the surface regeneration simply through polishing with a wet filter paper. Herein, regeneration of the electrode surface resulted in complete recovering of the peak height and remove the memory effect of the electrode.

3.2. Effect of pH

Cyclopentolate possess pKa value 8.42, therefore, the effect of the supporting electrolyte pH value is quite important. The influence of the pH on the CLO oxidation peaks applying ZY/CPE sensor was investigated at different pH values (Fig. 2). The peak potentials (E (V)) were shifted towards the negative direction indicating the rule of the proton in the oxidation reaction. The peak potentials were linearly related to the pH values in two ranges (E (V) = 1.288 – 0.0534 pH, r = 0.99987 at pH range 2-6 and E (V) = 1.01779 – 0.02394 pH, r = 0.98777, at pH range 7-12). The slope value was non Nernstian compliance assuming the participation of unequal electrons and protons in the oxidation reaction. Moreover, the peak current gradually increased with pH with the maximum value at pH 10.0, while higher pH value diminishes the peak current.

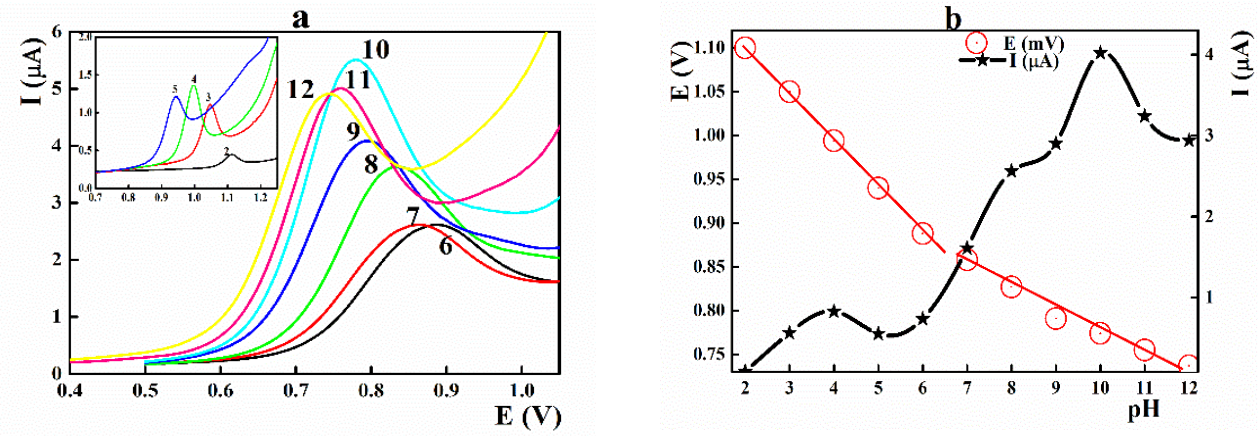


Figure 2. a) Differential pulse voltammograms of 275 ng mL^{-1} cyclopentolate at different pH values on 7.5 % zeolite based carbon paste electrode; b) peak currents and peak potentials against pH. Scan rate was 0.040 V s^{-1}

3.3. Effect of the scan rate

To explain the oxidation mechanism of cyclopentolate at the electrode surface, cyclic voltammograms were performed at the optimum pH with different scan rates ranging between 0.02 to 0.3 V with a step rate 0.02V (Fig. 3a). Under the assumption of a diffusion-controlled oxidation mechanism of CLO at the electrode surface, the CLO peak current gradually increased (r=0.9983) against the square root of the scan rate (r=0.9983) (Fig.3 b). In addition, plotting the log value of the scan rate (log υ) against the log values of peak current revealed a slope value about 0.56007 (Fig. 3 c) which sustain the diffusion mechanism.

The peak potential was shifted to the positive direction with the scan rates (Fig. 3d), indicating the irreversibility of the reaction [34-35]. The peak potential showed a linear relationship against the log value of the scan rate (Ep (V) =0.9791+0.0644 log υ (Vs^{-1}); r=0.9908). Based on the slope value and according to Laviron equation for the irreversible electrode reaction, 1.9788 electrons were involved in the present reaction [36].

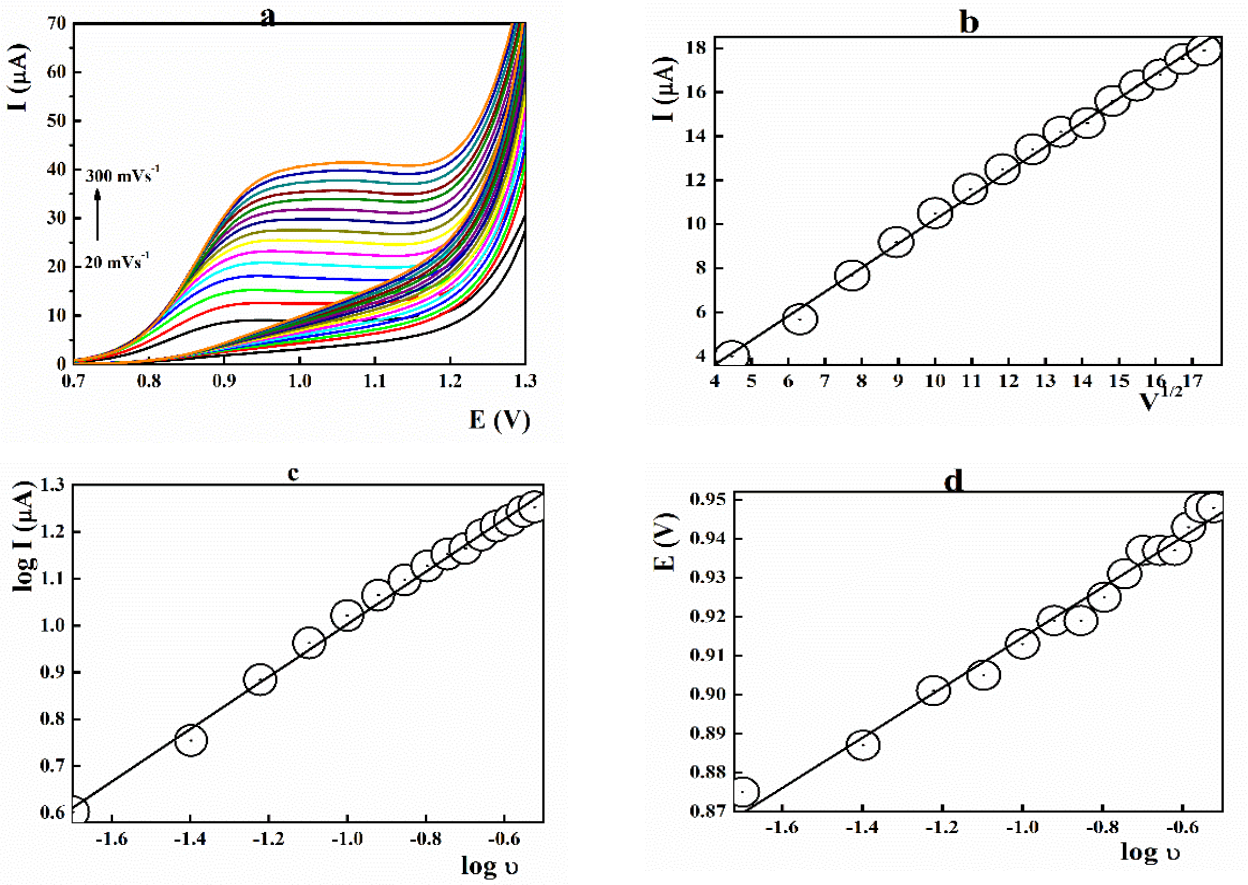
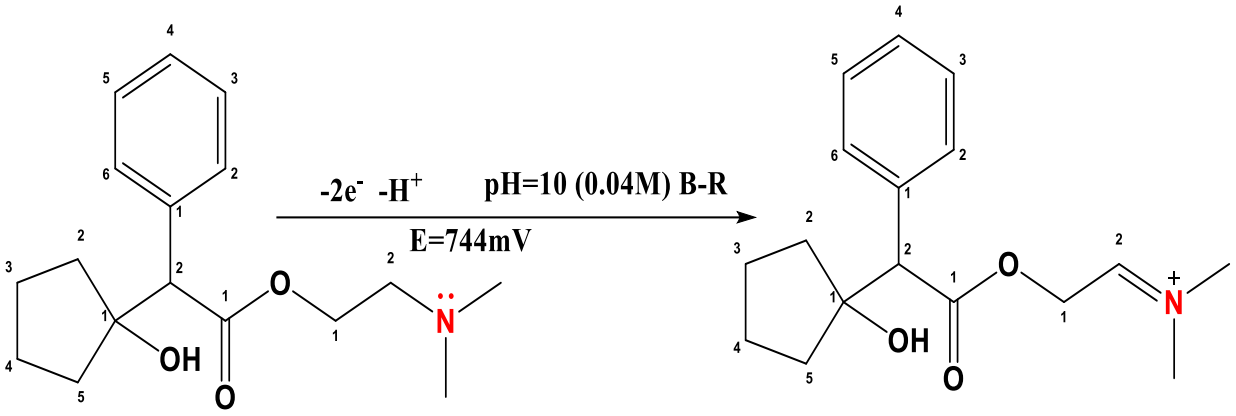


Figure 3. Voltammetric behavior of 275 ng mL^{-1} cyclopentolate at different scan rate values using 7.5% ZY/CPE at pH 10.0

For confirming the proposed reaction mechanism, computational molecular orbital calculations were applied (Fig. S3). Oxidation of the CLO takes place on the terminal amino group through transferring of one proton and 2 electrons (scheme 1).



Scheme 1. Computed reaction mechanism for the electrochemical oxidation of CLO at ZY/CPE surface

3.4. Analytical characterizations

Applying the optimized measuring parameters, aliquots of the CLO stock solution were added to the measuring cell at pH 10.0 and the voltammograms were recorded (Fig. 4). The peak current was compared to the concentration of CLO in ng mL^{-1}. The study findings (Table 1) show a high correlation coefficient with low standard deviation values, indicating that the recommended study protocol for cyclopentolate assaying is applicable (Table 1).

Table 1. Differential pulse voltammetry used to make the determination at pH10.0, cyclopentolate on ZY/CPE

Parameters	
Linear range (ng mL^{-1})	48.03-725.00
Slope (a) (µAcm^{-2})	0.016
s_a (µAcm^{-2})	0.001
Intercept (b) (µA mL ng)	0.649
s_b (µA mL ng)	0.072
$S_{y/x}$ (µA cm^{-2} mL ng)	0.154
Correlation coefficient (r)	0.9989
LOD (ng mL^{-1})	14.53
LOQ (ng mL^{-1})	44.03
RSD %	0.94
N	14
Intra-day repeatability (RSD %)	0.241
Inter-day repeatability (RSD %)	0.67
Electrode stability (RSD %)	0.735
Reproducibility of electrodes within-day[e]	1.15

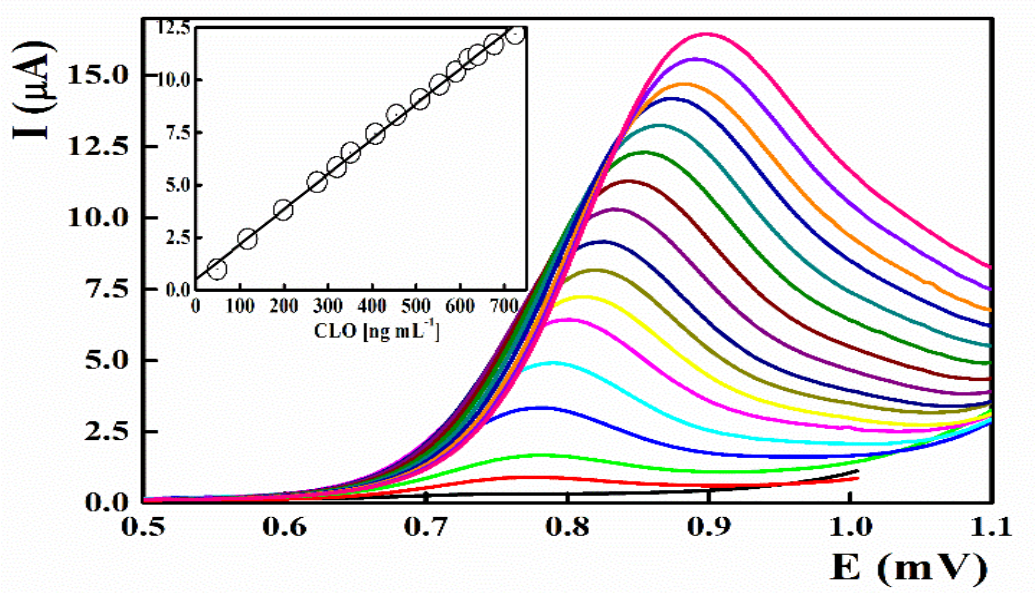


Figure 4. Differential pulse voltammetric determination of cyclopentolate using 7.5% ZY/CPE in BR buffer at pH 10.0 with scan rate 0.040V s^{-1}.

3.5. Stability and fabrication reproducibility

To performance of the fabricated ZY/CPE was monitored by recording the DPV signals for 275 ng mL^{-1} CLO over prolonged period. The fabricated sensor showed stable and reproducible oxidation peak current within the first 30 days with RDS 0.735% and 98% recovery of the peak height. The measuring repeatability was performed by measuring 10 replicate successive voltammograms for 275 ng mL^{-1} CLO. High measurement repeatability with standard deviations of 1.15% was acheived.

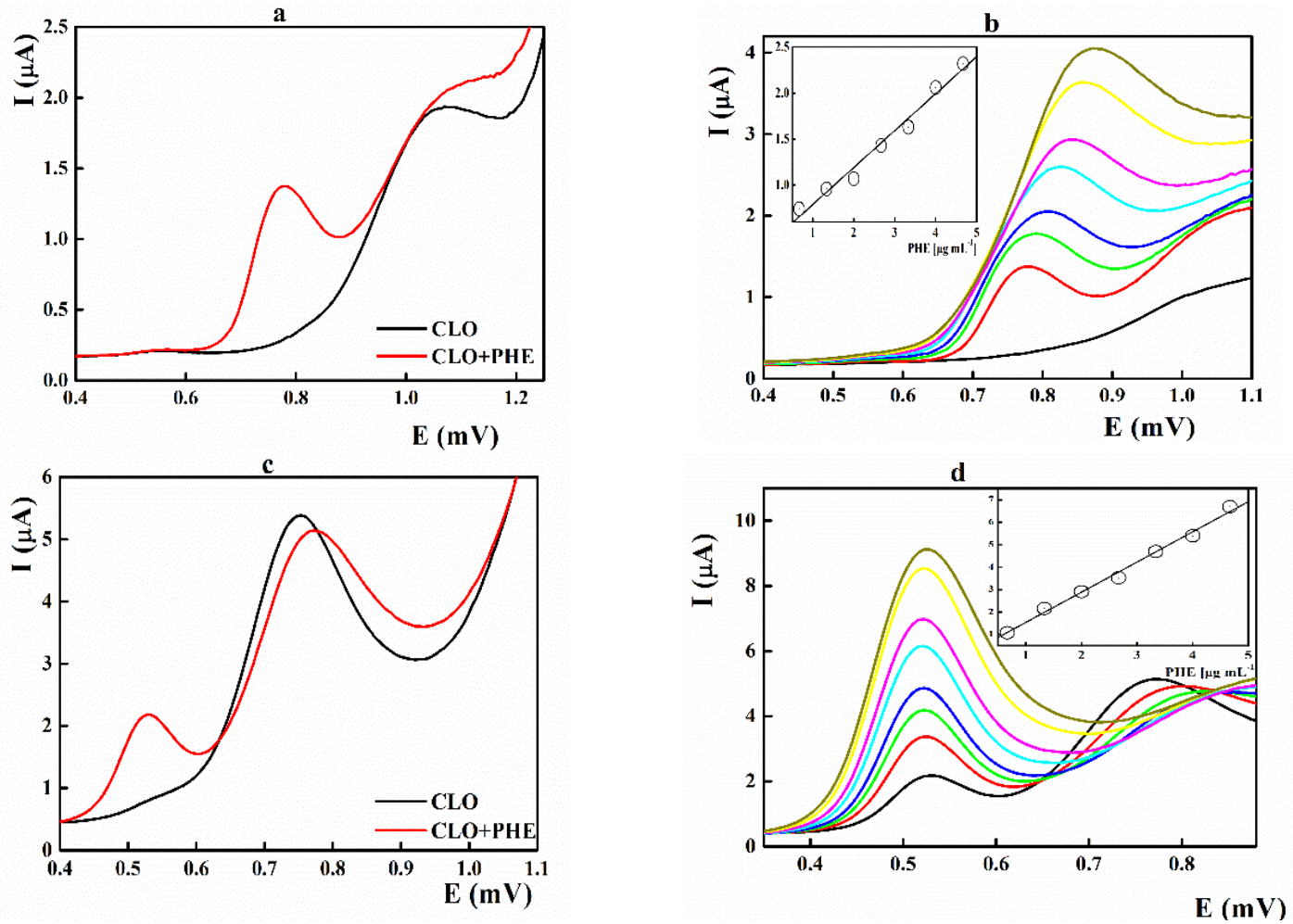
The fabrication reproducibility was performed by recording the signal of five ZY/CPEs towards 275 ng mL^{-1} of cyclopentolate. Acceptable RSDs of 2.0% was achieved confirming the high reproducibility and repeatability of the fabrication protocol.

3.6. Specify and interference

In addition to the main active ingredient, pharmaceutical formulations may contain variety of additives, excipients, and sometimes a combination of two active ingredients together in the same dosage form. Combination of both phenylephrine hydrochloride (PHE) and cyclopentolate hydrochloride (CLO) in eye drops are usually used in ophthalmic operations; hence, the interference of phenylephrine is quite crucial for the analysis of real samples contain both active ingredients.

Voltammograms for the measuring solution containing both phenylephrine and cyclopentolate at pH 6 (optimum for PHE [37]) was represented in figure 5a. At such pH value, sharp and reproducible peak was achieved for PHE at 0.77 V with linear relation of high correlation coeffecient [I_p (μA)=0.38845+0.40142 PHE [μg mL^{-1}], R=0.989586] with a broad CLO peak at 1.04V (Fig. 5 a, b). Switching the pH value to 10 (optimum for CLO), PHE showed a noticeable peak at 0.522 V while

those for CLO was recorded at 0.79 V with more than 0.27 V between the two peaks confirming the possibility of simultaneous determination of both CLO and PHE (Fig. 5 c). Applying the proposed sensors, improved sensitivity was recorded for PHE [I_p (µA)=0.19336+1.34612 PHE [µg mL^{-1}], R=0.9961] compared with that at pH6 (Fig. 5 d). Moreover, at such pH, reproducible CLO differential pulse voltammograms were achieved [I_p (µA)=-0.7279+0.01408 CLO [ng mL^{-1}], R=0.99202] but with somewhat broad peaks due to the posing of the electrode with PHE and/or its oxidation products (Fig. 5 e).



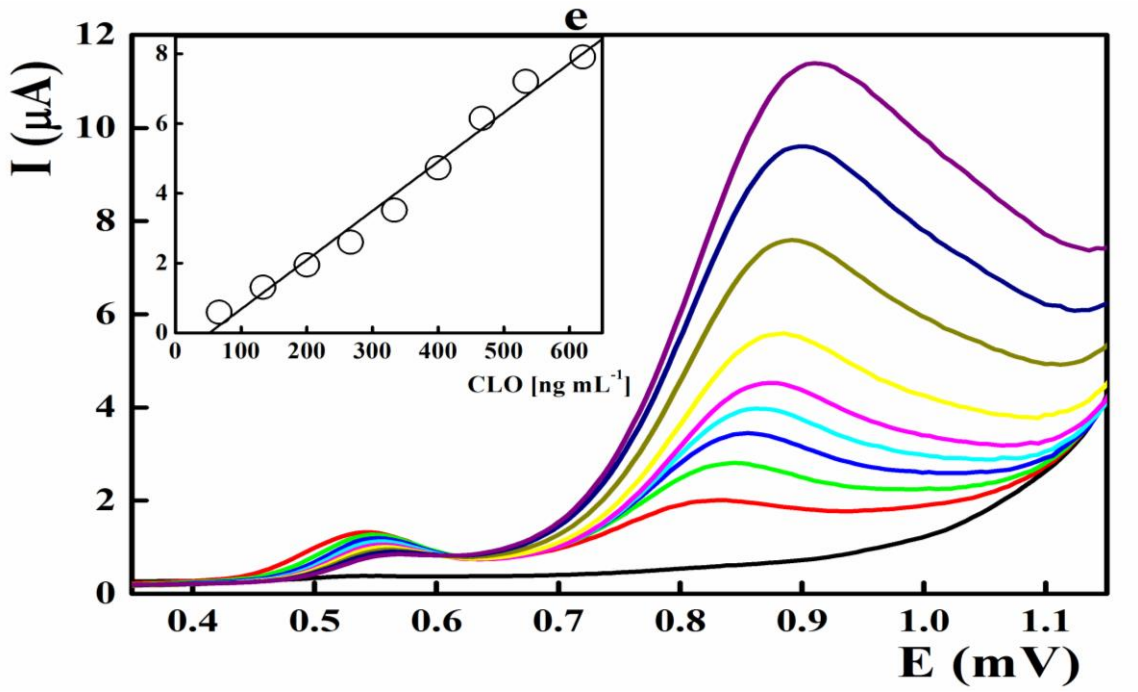


Figure 5. Simultaneous voltammetric determination of cyclopentolate and phenylephrine on 7.5% zeolite based carbon paste electrode; a, b) at pH 6.0, c, d) at pH 10.0; e) differential pulse voltammetric determination of CLO on Zy/CPE at pH 10.0 in presence of phenylephrine

According to the producer specifications, Pentolate and Swixolate (cyclopentolate 1% eye drops) contain other excipients such as EDTA disodium salt, boric acid, methylparaben, propylparaben (as preservative), potassium chloride, sodium carbonate/hydrochloric acid and completed with water. High tolerance limit (more than 100 fold) of the aforementioned additives was achieved; therefore, the proposed analysis protocol can be successfully applied for assaying of cyclopentolate in real samples.

Cyclopentolate degraded rapidly in basic medium with the formation of N-N-dimethylaminophenol, phenylacetic acid, (1-hydroxycyclopentyl) benzeneacetic acid, and β-hydroxy acid [26]. None of these degradation products resulted in a noticeable interference and cyclopentolate was assayed freely from interference of its degradation products.

3.7. Analysis of pharmaceutical samples

The practical applicability of the proposed analysis protocol was explored by assaying the cyclopentolate in different eye drop sample. The samples were analyzed according to pharmacopial protocol with chromatographic techniques and referred to the provided sensors after sufficient dilution. High recoveries with acceptable relative standard deviation values revealed the suitability of the proposed analysis protocol for assaying of cyclopentolate in different pharmaceutical formulation in presence or absence of phenylephrine (Table 2).

Table 2. Analysis of cyclopentolate in eye drop dosage forms

Sample	Pentolate			Cyclophrine		
Analysis protocol	Present*	Bias %	HPLC*	Present*	Bias %	HPLC*
% Found	100.8	2.0	100.9	99.98	3	99.95
	99.6	2.0	100.1	100.4	1.2	100.1
	100.5	3.0	99.4	100.2	2	99.96
Mean±S.D.	100.13±0.56		100.27±0.41	100.19±0.04		100.00±0.01
t-test (Critical=2.77)		0.41			1.45	
F-test (Critical=19)		1.36			6.27	

* Average of three replicates.

4. CONCLUSION

A zeolite-based carbon paste sensor was developed as a novel sensor for voltammetric assessment of cyclopentolate for the first time in this paper. Zeolite modulation results in efficient electrocatalytic operation for cyclopentolate electrochemical oxidation. The cited electrode showed linear relation in the CLO concentration ranged from 48.03 to 725 ng mL^{-1} with LOD 14.53 ng mL^{-1}. Oxidation mechanism of cyclopentolate was elucidated electrochemically and with molecular orbital calculation studies. In particular, the influence of inteferents and degradation products on the simultaneous voltammetric identification of cyclopentolate and phenylephrine was explored. In comparison to traditional HPLC techniques, the advanced sensitivity and selectivity of the fabricated sensors allowed for a specific voltammetric protocol to be used in eye drop samples.

SUPPLEMENTARY MATERIAL

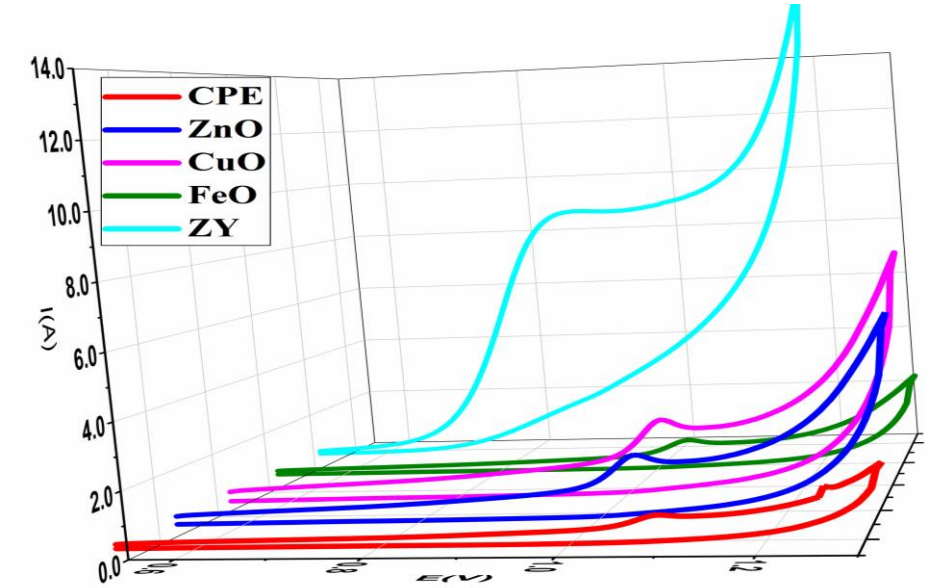


Figure S1. Voltammetric behavior of 275 ng mL^{-1} cyclopentolate using carbon paste electrode modified with different nanostructures at pH 10.0. Scan rate 40 mV s^{-1}.

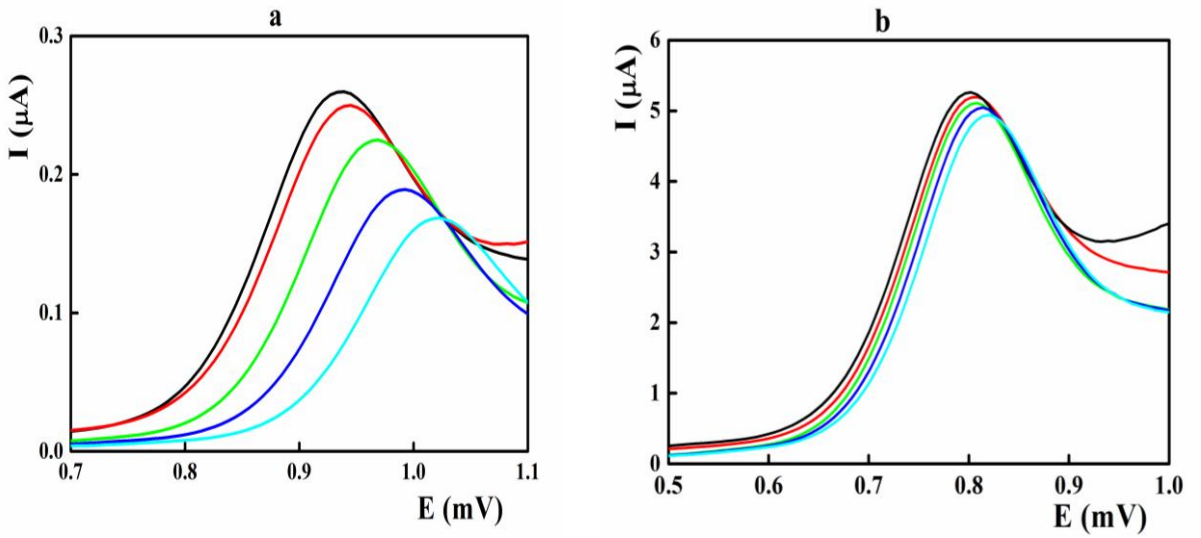


Figure S2. Successive differential pulse voltammograms of 275 ng mL^{-1} CLO on 7.5% zeolite based carbon paste electrode at pH 10.0. Scan rate 40 mV s^{-1}

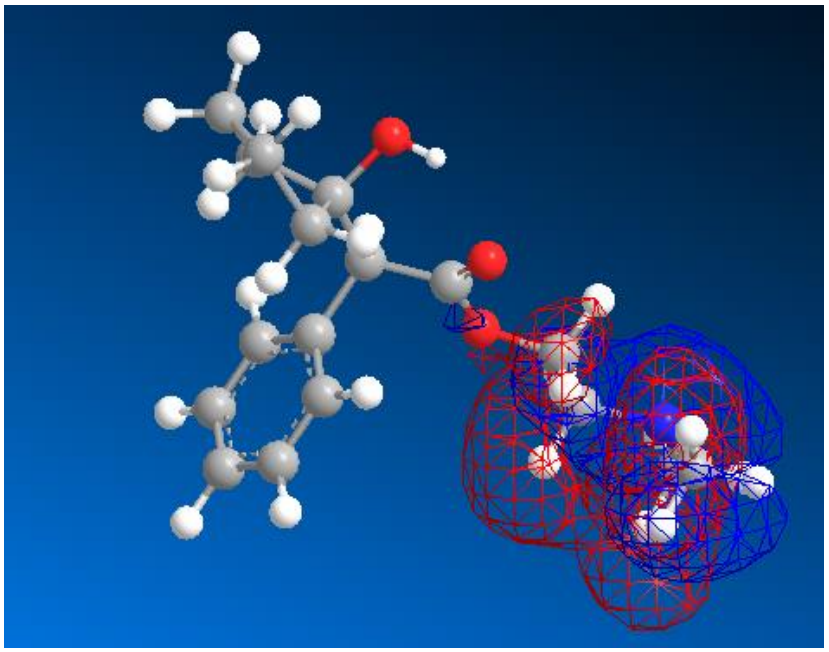


Figure S3. Molecular structure of cyclopentolate

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COMPETING INTERESTS
The authors declare no conflict of interest.

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