

## Research Article

# Cyclic Voltammetric Investigation of Caffeine at Anthraquinone Modified Carbon Paste Electrode

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Electrochemical methods have been widely used for the determination of electroactive compounds due to their simplicity, sensitivity, stability, and low cost. A carbon paste electrode was modified with anthraquinone. Cyclic voltammetry (CV) was employed to study the properties of the modified electrode toward the oxidation of caffeine (CAF). Compared to the unmodified electrode, the AQMCPE showed excellent catalytic activity for the oxidation of caffeine. AQMCPE was used to determine CAF in drug samples electrochemically. SWV was used to plot the calibration curve and there was a good linear relationship between anodic peak current and CAF concentration in the range  $2.0 \times 10^{-6} - 8.0 \times 10^{-4}$  M, with the correlation coefficient of 0.998 and a detection limit of  $1.43 \times 10^{-7}$  M. The application of the modified electrode for the determination of CAF in pharmaceutical formulation showed good recovery with reproducible results.

## 1. Introduction

Caffeine (3,7-dihydro-1,3,7-trimethylxanthine-1H-purine-2,6-dione) is a naturally occurring alkaloid that belongs to a family of organic compounds known as methylxanthines [1, 2]. It is a heterocyclic amine found in many plant materials including the tea leaves, coffee beans, kola nuts, cocoa, and beans as major constituent and believed to protect the plants from insects [3–7]. Due to its stimulant properties, caffeine is used almost in all countries of the world in the form of dietary products such as coffee, tea, soft drinks, and chocolates. Caffeine (CAF) stimulates central nervous and cardiovascular systems [8]. It affects the brain and results in a relaxed mood, decreased fatigue, increased focus, and faster, and clear thoughts. Moderate consumption of caffeine, help in reducing the risks of several chronic diseases like Diabetes, Parkinson's diseases, liver disease, and colon cancer, as well as improve immune function [9]. However, excess consumption of CAF cause trembling, nausea, nervousness, and mutational effects such as inhibition of DNA [10]. Caffeine is also considered to be a risk factor for

a cardiovascular disease, asthma, kidney malfunction, and may affect behavior by causing depression and hyperactivity [3, 11].

Several methods-including UV [12], HPLC [13], NMR [14], capillary electrophoresis [15], TLC [16], and GC [17] have been reported for the determination of caffeine in pharmaceutical formulations, biological samples, and food stuffs. Most of the methods are either expensive or have time consuming procedure like preconcentration or multisolvent extraction and require highly skilled technicians [2–4, 18]. Thus, development of an easy, accurate, reliable, and cheap technique for determination of CAF is an important requirement of present days.

This fact, in recent years, has diverted the attention of most of the electrochemists towards electrochemical methods because of their simplicity, large sensitivity, excellent stability, low cost instrumentation, and onsite monitoring [18] and has been widely used to study the redox behavior of electroactive compounds. But, the electroanalysis of caffeine at the surface of common electrode materials (like metals and bare carbon electrodes) is not that effective, because

the oxidation of CAF occurs at more positive potential which in most cases overlaps with the discharge of background medium [11]. Several solutions have been proposed including the choice of anodic potential, supporting electrolyte or modified electrodes [19]. The reported electrochemical methods including graphite pencil electrode [20], nafion-ruthenium oxide pyrochlore modified glassy carbon electrode [21], multi-walled carbon nanotube and nafion modified glassy carbon electrode [22], carbon fiber ultra-microelectrode [23, 24], nafion and graphene oxide modified glassy carbon electrode [11], and benzoquinone modified carbon paste electrode [3].

Carbon paste electrodes belong to promising electrochemical or bio-electrochemical sensors of wide applicability. The ease of preparation, speed of getting a new reproducible surface, low residual current, porous surface, low cost, and so forth are some of the advantages of CPEs over all other carbon electrodes. It also has been shown that carbon paste electrodes exhibit compatibility to biological systems higher than that of other commonly used electrode materials [25].

Probably, electrochemical determination of caffeine at the anthraquinone modified carbon paste electrode (AQMCPSE) has not been reported, yet. The ability of this new modified carbon paste electrode toward the oxidative behavior of caffeine has been evaluated using cyclic voltammetric technique in the present investigations. The modified electrode was employed for the determination of caffeine in commercial caffeine containing tablets. The proposed sensor exhibits high sensitivity, good reproducibility, long-term stability, and remain uninfluenced from interfering species like matrices present in the tablets.

## 2. Experimental Method

**2.1. Reagents and Apparatus.** Caffeine (anhydrous, 98.9% HPLC grade) was obtained from Addis Pharmaceuticals Factory (APF), Ethiopia. Anthraquinone (LOBA, India), graphite powder (BDH, England), paraffin oil (Nice, India),  $\text{HClO}_4$  (BDH, England), NaOH (Scharlau, Spain), HCl (Nice, India), Paramol-c (Franklin laboratories, India), Nicip cold (Cipla Ltd., India), and No cold (Cipla Ltd., India) were used during the experiment. All chemicals were of analytical grade and used without further purification. Stock solution of caffeine (1 mM) was prepared in 0.1 M  $\text{HClO}_4$  solution of pH 0.56. Working standard solutions of lower concentration were prepared by dilution method using the supporting electrolyte. NaOH (0.1 M) and HCl (0.1 M) were used for adjusting the pH of the solution. Aqueous solutions were prepared using double distilled water.

Electrochemical experiments were performed using a BASCV-50W electrochemical analyzer (Bioanalytical system Inc., USA) with a conventional three electrode cell. An unmodified or anthraquinone modified, carbon paste electrode (AQMCPSE) was used as working electrode. Silver-silver chloride and a copper wire were used as a reference and an auxiliary electrode, respectively. All the pH values were measured with bench microprocessor pH meter (HANNA Instruments, Italy) which was calibrated with a standard

buffer solution (pH = 4.01 and pH = 7.01). All measurements were carried out at room temperature at  $25 \pm 0.2^\circ\text{C}$ .

**2.2. Preparation of Bare Carbon Paste Electrode (BCPE).** The BCPE was prepared as follows: 70% (w/w) graphite powder and 30% (w/w) paraffin oil ( $d = 0.88 \text{ g cm}^{-3}$ ) were homogeneously mixed by hand for 30 minutes using pestle and mortar [26]. The homogenized paste was allowed to rest for a minimum period of 24 hrs [3], and then the paste was packed into the tip of the plastic syringe. The surface of the electrode was smoothed on weighing paper and a copper wire was introduced from the back side of the syringe to provide electrical contact.

**2.3. Preparation of Modified Carbon Paste Electrodes.** Anthraquinone modified carbon electrode (AQMCPSE), that is, new sensor, was prepared by mixing 2.015 g of graphite powder with 0.15 g of anthraquinone in a small agate mortar for about five minutes. In this mixture 0.825 g of paraffin oil was added and then milled again for 30 min to obtain a homogenous 5% (w/w) anthraquinone modified carbon paste. The homogenized paste further was allowed to rest for 24 hrs. Various modified carbon pastes containing different mass percentage of anthraquinone (10, 15, 20, and 25% w/w) were prepared in the same way. A desired amount of the prepared carbon paste was packed into the end cavity of the syringe. The surface of the fabricated anthraquinone carbon paste electrode was then polished on a clean paper before experimentation.

**2.4. Real Sample Analysis.** The proposed method was exploited for the determination of caffeine in three commercially available caffeine tablets. Ten pieces of three brands of caffeine tablets were accurately weighed and grounded into powder using mortar and pestle. An adequate amount of the homogenous powder, corresponding to the amount of one tablet for each brand, was weighed and transferred into separate 100 mL volumetric flask and completed up to the mark with distilled water. After filtration, sufficient amount of the clear solution was diluted with perchloric acid, so that its concentration falls within the linear working range. Cyclic voltammograms were obtained by scanning the potential from 600 to 1700 mV versus Ag/AgCl electrode. The amount of caffeine content in the different brands of caffeine tablets has been determined using calibration method.

## 3. Results and Discussion

**3.1. Electrochemical Behavior of Caffeine at CPE.** The electrochemical behavior of caffeine at CPE was investigated using cyclic voltammetry. Figure 1 shows the cyclic voltammograms obtained for caffeine (1 mM) at the AQMCPSE (a) and UMCPE (b), in 0.1 mol L<sup>-1</sup>  $\text{HClO}_4$  (pH 0.56) with a scan rate of 100 mVs<sup>-1</sup>. The electrochemical response of caffeine showed one broad anodic peak centered at about 1612 mV versus Ag/AgCl at the unmodified CPE. Under similar conditions, a sharp peak at 1527 mV has been obtained at the AQMCPSE. The potential shift towards less positive direction

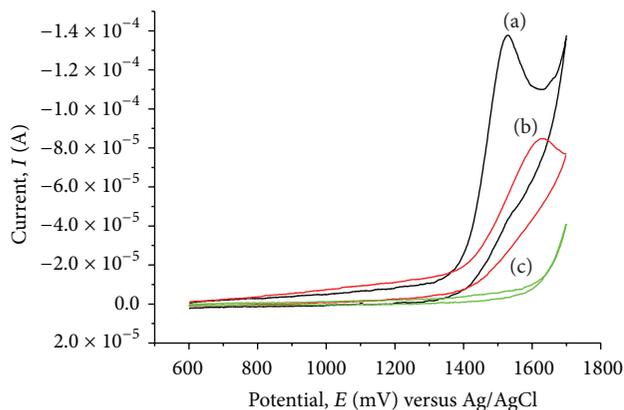


FIGURE 1: Cyclic voltammograms: (a) AQMCPE, (b) UMCPE, in the presence of 1 mM CAF in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  (pH 0.56), at a scan rate of  $100 \text{ mVs}^{-1}$ , and (c) AQMCPE in the absence of 1 mM CAF.

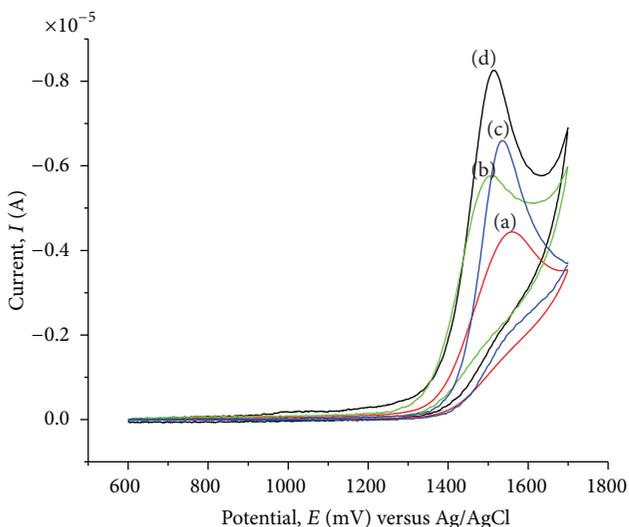


FIGURE 2: CVs of AQMCPE in 0.1M of different supporting electrolytes (a) acetate, (b) phosphate, (c) sulfuric acid, and (d) per-chloric acid in the presence of 1 mM caffeine; at a scan rate of  $100 \text{ mV/s}$

accompanied by the remarkable peak current enhancement from  $6.42 \times 10^{-5} \text{ A}$  at the unmodified CPE to  $1.37 \times 10^{-4} \text{ A}$  at the modified CPE is clear evidence of the catalytic effect of the modified CPE toward caffeine oxidation. Also, there is no appearance of any reduction peak in the reverse scan, this indicate that the present electrochemical process is irreversible in nature.

Comparing the cyclic voltammograms of AQMCPE in the presence (b) and absence (c) of 1 mM caffeine, in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  solution, at a scan rate  $100 \text{ mVs}^{-1}$ , it is revealed that the observed peak is exclusively due to oxidation of caffeine and there was no redox peak of AQMCPE in the blank solution. From these observations it can be concluded that, the background current of the supporting electrolyte

has no interfering signal during the electrochemical measurements on the AQMCPE in the potential window between 600 mV and 1700 mV.

**3.2. Influence of Supporting Electrolyte.** Preliminary experiments were performed to select the best supporting electrolyte for the oxidation of caffeine (the mechanism of the process is displayed in Scheme 1). Various types of 0.1 M acids or buffers such as perchloric acid, sulfuric acid, phosphate buffer, and acetate buffer were tested as possible supporting electrolytes, as shown in Figure 2. An excellent peak response and reproducibility of the signals in solutions of perchloric acid enabled us to select it as a best supporting electrolyte for the sensors working in current experiment.

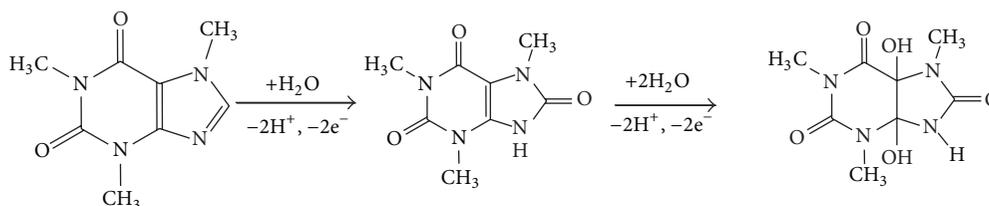
**3.3. Effect of pH.** The pH value of an electrolyte solution is an important factor that affects the redox behavior of electroactive species [27]. So, the effect of variation of pH for the oxidation of  $1.0 \times 10^{-3} \text{ M}$  caffeine was studied, employing CV technique, within strong acidic pH range (i.e., 0.50 to 3.10) using perchloric acid solution as supporting electrolyte, at a scan rate  $100 \text{ mVs}^{-1}$ . NaOH (0.1 M) and HCl (0.1 M) were used for adjusting the pH of the solution. As indicated in Figure 3, the anodic peak potential of caffeine shifted toward less positive direction as the pH increases from 0.5 to 3.10. This observation is strong evidence that reflects the involvement of protons in the electrode process. The linear relationship between pH and  $E_{pa}$  ( $dE/d(\text{pH}) = 46.8 \text{ mV}$ ) reveals that equal number of protons and electrons are involved in the oxidation process of caffeine within the studied pH range.

Hence, the overall process involves four protons and four electrons as suggested by Dryhurst and Hansen [28].

The first step is a  $2\text{H}^+$ ,  $2\text{e}^-$  oxidation of the C-8 to N-9 bond to give the substituted uric acid. This is followed by an immediate  $2\text{H}^+$ ,  $2\text{e}^-$  oxidation to the 4,5-diol analog of uric acid, which rapidly fragments.

The effect of variation of pH on the peak current of the electrocatalytic oxidation of caffeine at AQMCPE was also studied. The peak current decreased linearly with increase in solution pH (Figure 4). However, better shape of voltammogram and excellent peak response were obtained at pH 0.56. Based on this fact, pH 0.56 was used as a suitable medium for further investigation.

**3.4. Effect of Electrode Composition.** Cyclic voltammograms of 1 mM caffeine in perchloric acid solution (pH 0.56) at carbon paste electrode modified with various mass percentages (%w/w) of anthraquinone was recorded at a scan rate of  $100 \text{ mVs}^{-1}$ . The composition of the modifier (i.e., anthraquinone) greatly influences the oxidation of caffeine at the carbon paste electrode. As shown in Figure 5, the magnitude of peak current increased upon the increase of the amount of anthraquinone in the CPE up to 15% (w/w) and then decreased. The decreased peak current may be attributed to the decrease of conductivity of the electrode with the increase of percentage of less conductive anthraquinone and decrease in the percentage of the more conductive graphite



SCHEME 1: Mechanism for the electrochemical oxidation of caffeine.

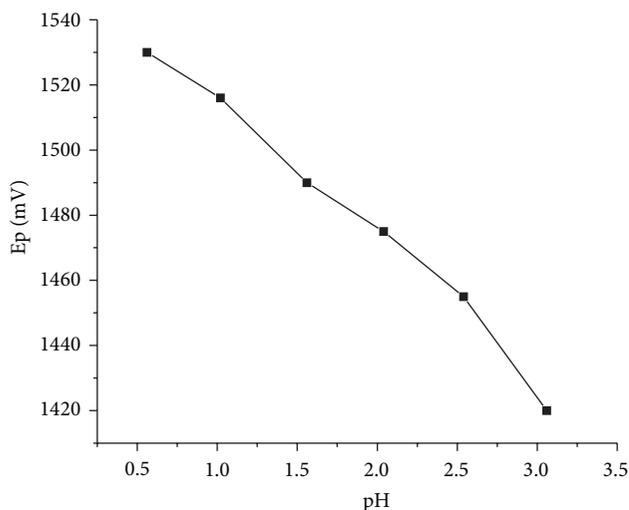


FIGURE 3: Effects of variation of pH on the anodic potential of 1 mM caffeine.

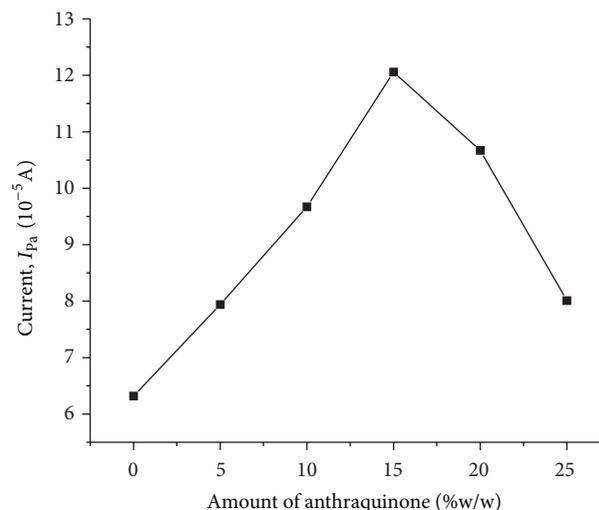
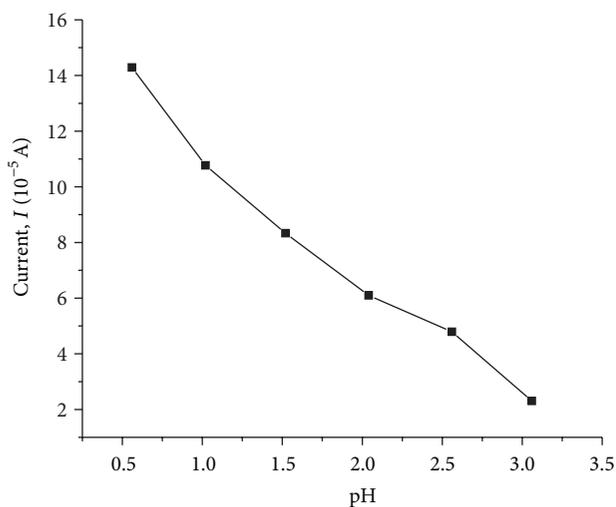
FIGURE 5: Effect of the amount of anthraquinone on the anodic peak current of 1 mM caffeine, in 0.1 M HClO<sub>4</sub> (pH 0.56); at scan rate of 100 mV/s.

FIGURE 4: Effect of pH on the anodic peak current of 1 mM caffeine.

powder. Therefore, based on the maximum current response, 15% (w/w) of AQMCPE was used for the subsequent electrochemical study.

**3.5. Effect of Scan Rate.** The effect of scan rate on the oxidation peak potential ( $E_{pa}$ ) and peak current ( $I_{pa}$ ) of caffeine at

AQMCPE was examined by cyclic voltammetry by varying the sweep rate from 20–500 mVs<sup>-1</sup>. Figure 6 indicates the CVs of  $1.0 \times 10^{-3}$  M caffeine in perchloric acid solution (0.1 M, pH 0.56) at a scan rate ranging between 20 and 500 mVs<sup>-1</sup>. The electrode reaction was irreversible as shown from the lack of a reduction peak in the cyclic voltammogram. This was also further confirmed by the shift of peak potential toward more positive value with increasing scan rate.

As depicted in Figure 6, the peak current increased with increase of scan rate and due to excellent peak response, a scan rate of 100 mVs<sup>-1</sup> was chosen for subsequent determinations. The peak current of caffeine showed linear dependence on the square root of scan rate ( $v^{1/2}$ ), as shown in Figure 6. The regression equation was  $I_{pa} (\mu A) = -0.469 + 0.594 v^{1/2}$  ( $R^2 = 0.999$ ). These results indicate that the electrode process is diffusion controlled. Further evidence for the nonadsorptive behavior of caffeine was obtained, when the working electrode was switched to a medium containing only supporting electrolyte after being used in voltammetric measurements of caffeine solution, no voltammetric signal was observed. This result was in agreement with the data previously reported [2, 18, 27].

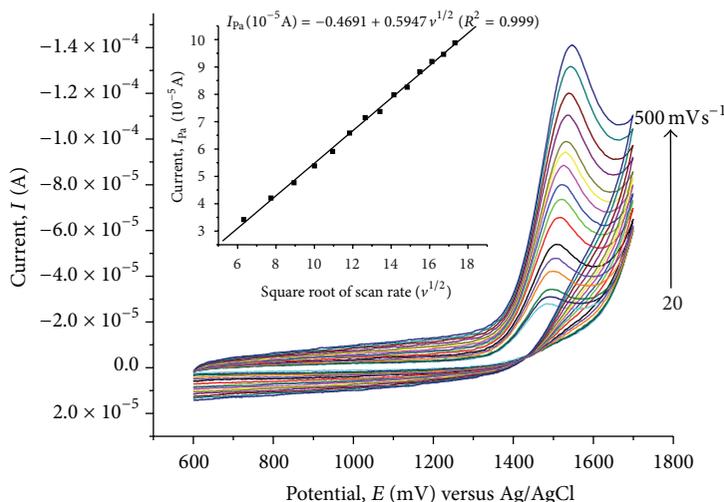


FIGURE 6: Cyclic voltammograms of AQMCPE in  $\text{HClO}_4$  (pH 0.56) containing 1 mM of caffeine, at scan rate of 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 350, 400, 450, and 500 mV/s (inset Plot of  $I_p$  (A) versus  $v^{1/2}$  mV/s).

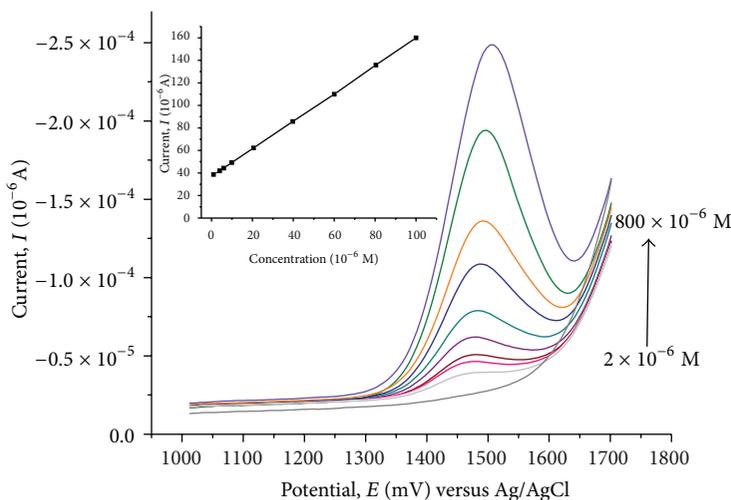


FIGURE 7: SWVs of AQMCPE in 0.1 M  $\text{HClO}_4$  (pH 0.56) for different concentration of caffeine (2, 4, 6, 10, 20, 40, 60, 80, 100, 300, 500, and 800  $\mu\text{M}$ ) at optimized parameters (inset is the linear calibration plot between peak current and concentration of caffeine in the range of 2–800  $\mu\text{M}$ ).

According to simplified Randles-sevik's equation ( $I_p = \text{constant} \times v^{1/2}$ ), a linear plot of  $\log I_p$  versus  $\log v$  was obtained with the corresponding equation:

$$\log I_p = -5.3335 + 0.5356 \log v, \quad R^2 = 0.997. \quad (1)$$

The slope value of 0.5356 was close to the theoretically expected value of 0.5 for a purely diffusion controlled process, which, further confirms that the electrocatalytic oxidation process of caffeine at anthraquinone modified carbon paste electrode is controlled by diffusion which received a good support from the literature [29].

**3.6. Calibration Curve.** Calibration curve was used for determining the concentration of caffeine in the real samples. SWV was employed to plot calibration curve, because the peaks are

better defined at lower concentration of caffeine compared to cyclic voltammetry. Under the optimized solution and method parameters, the SWVs of different concentration of CAF are shown in Figure 7. The SWV current response was linearly varied with the concentration of CAF in the range 2–800  $\mu\text{M}$  (Figure 7). The linear regression equation and correlation coefficient were  $I_p$  ( $\mu\text{A}$ ) = 37.08 + 1.826C ( $\mu\text{M}$ ) and 0.998, respectively. The limit of detection (LOD) was  $1.43 \times 10^{-7}$  M ( $n = 12$ ). The limit of detection was calculated using the following formula [26] and nine blank measurements were carried out.

Consider

$$\text{LOD} = \frac{3S}{m}, \quad (2)$$

TABLE 1: Determinations of caffeine in pharmaceutical tablets using CV.

Sample	Labeled amounts (mg)	Detected amount (mg) <sup>a</sup>	Recovery/%
No cold	25	23.05 ± (1.38)	92.22
Nicip cold	30	29.34 ± (0.69)	97.80
Paramol-c	30	28.94 ± (0.98)	96.46

<sup>a</sup>Mean value ± standard deviation ( $n = 5$ ).

where  $S$  is standard deviation of the blank and  $m$  is slope of the calibration curve.

### 3.7. Analytical Application

**3.7.1. Real Sample Analysis.** The applicability of the developed method for the determination of caffeine in real sample was investigated by cyclic voltammetry. The procedure for the tablet analysis was followed as described in the sample preparation section. The experimentally detected values and the labeled values are compared in Table 1 and it is found that the results obtained using AQMCPE are in a good agreement with the content labeled.

**3.7.2. Reproducibility and Stability of the Modified Electrode.** The reproducibility of the fabricated electrode was investigated by cyclic voltammetry. The relative standard deviation (RSD) obtained for five successive determination of  $1.0 \times 10^{-3}$  M caffeine at AQMCPE was 2.8%, which showed that the electrode gave good reproducibility. After several days of repeated use, no significant difference in the response of the electrode was observed, indicating the electrode was stable. After the electrode was stored in the laboratory at room temperature for 30 days, it could retain 92.6% of its original response, suggesting acceptable storage stability. Furthermore, three AQMCPE were prepared under the same condition and then determination of  $1.0 \times 10^{-3}$  caffeine was performed on each electrode. The RSD of the peak current for triplicate measurements was 3.68% indicating good reproducibility of the fabrication method of the electrode.

The developed electrochemical sensor can be used as an alternative method for the quantification of caffeine in real samples because of its simplicity and low cost instrumentation compared with other ones such as HPLC.

## 4. Conclusion

This work demonstrates the ability of AQMCPE for the electrochemical investigation of caffeine and determination of caffeine. The results obtained illustrates that the electrocatalytic oxidation of caffeine at the surface of the modified electrode occurs at a potential about 82 mV less positive than at a bare carbon paste electrode. The anodic peak current of caffeine was proportional to the concentration in the range  $2.0 \times 10^{-6}$  to  $1.0 \times 10^{-4}$  M using SWV, with a detection limit  $1.43 \times 10^{-7}$  M and correlation coefficient of 0.998. Moreover, simple preparation, good stability, excellent reproducibility,

sensitivity, low cost, and rapid analysis make the developed method suitable for the electrochemical investigation and routine determination of caffeine in real samples such as pharmaceutical formulation.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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