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Polymer modified glassy carbon electrode for the electrochemical determination of caffeine in coffee

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ABSTRACT

4-Amino-3-hydroxynaphthalene sulfonic acid (AHNSA) was electropolymerized on a glassy carbon electrode. The deposited film showed electrocatalytic activity towards the oxidation of caffeine. The polymer-modified electrode showed high sensitivity, selectivity and stability in the determination of caffeine in coffee. The peak current increased linearly with the concentration of caffeine in the range of 6×10^{-8} to 4×10^{-5} mol L^{-1}, with a detection limit of 1.37×10^{-7} mol L^{-1} (LoD = 3δ/slope). Analysis of caffeine in coffee was affected neither by sample matrices nor by structurally similar compounds. Recoveries ranging between 93.75 ± 2.32 and 100.75 ± 3.32 were achieved from coffee extracts indicating the applicability of the developed method for real sample analyses.

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1. Introduction

Caffeine (1,3,7-trimethylxanthine) is a naturally occurring alkaloid that is widely found in plant products and beverages. It is a natural stimulant contained in coffee, tea, chocolate, soft drinks and can also be purchased in capsules or tablets for the treatment of asthma, nasal congestion, headache or to improve athletic endurance and facilitate weight loss [1]. Almost half of the caffeine consumers ingest caffeine from multiple sources [2,3], the caffeine content of which varies with the type of source [4–6].

In human and animal studies, caffeine produces mental and behavioral effects that are similar to those of typical psychomotor stimulant drugs (*e.g.*, amphetamine and cocaine) [7]. Stimulation of the central nervous system, diuresis and gastric acid secretion are the most studied physiological effects caused by caffeine [1]. Habitual coffee and tea drinkers also experience increase in blood pressure when consuming caffeine at the doses found in the commonly consumed beverages; tea, coffee, cola soft-drinks and energy drinks as well as in many pharmaceuticals [8]. Since the caffeine content in coffee is the highest of the common sources [5], a sensitive, fast, selective and inexpensive analytical method for determining caffeine in coffee is highly needed.

Many methods, including high performance liquid chromatography [9,10], capillary chromatography [11], capillary electrophoresis [12], spectroscopy [13,14] and liquid chromatography–tandem mass spectroscopy [15] have been reported for the determination of caffeine in coffee, tea and cola beverages. Usually, these methods demand expensive apparatus, highly skilled technicians, complicated and time-consuming procedures. Compared to these conventional analytical methods, electroanalytical methods are rapid, convenient, of low-cost and environmental-friendly [16].

Polymer-modified electrodes (PMEs) have received considerable attention in recent years due to their good stability, reproducibility, increased active sites, homogeneity in electrochemical deposition and strong adherence to the electrode surface [17–19]. However, among the electroanalytical methods recently reported for the determination of caffeine [20–29], a single work was published based on electropolymerized polymer-modified electrode which could be because of the high interfering back ground current at its oxidative potential [20].

Hence, we planned to develop a polymer-modified electrode that lowers the oxidation potential of caffeine for its determination without a significant influence from background current. To the best of our knowledge, the use of poly(AHNSA) modified GCE for the electroanalytical detection of caffeine is not reported. Hence, we report the preparation of a sensor obtained by electropolymerizing 4-amino-3-hydroxynaphthalene-sulfonic acid (AHNSA) (Scheme 1(b)) at glassy carbon electrode and its application for the determination of caffeine in coffee.

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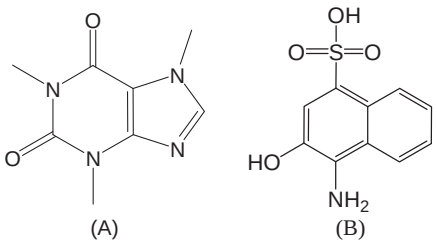


Scheme 1. The chemical structure of caffeine (A) and 4-amino-3-hydoxynaphthalene sulfonic acid (B).

2. Experimental

2.1. Instruments and reagents

Voltammetric experiments were carried out using CHI760D Electrochemical Workstation, CH Instruments (Austin, Texas, USA). All electrochemical experiments were performed employing a conventional three-electrode system with a glassy carbon electrode (3 mm in diameter) or a poly(AHNSA) modified glassy carbon electrode as the working electrode, platinum wire as an auxiliary electrode and Ag/AgCl electrode as a reference electrode. All experiments were carried out at $20 \pm 2\,^{\circ}C$. Caffeine solutions were prepared from standard caffeine supplied by Fischer Scientific Limited. All other reagents were of analytical grade and were used directly without further purification. Distilled water was obtained by purification through a Millipore water system and was used throughout.

2.2. Fabrication of the poly(AHNSA) modified glassy carbon electrodes

Poly(AHNSA) modified GCE was prepared as reported in our previous work [30]. Briefly, the GCE was first rinsed with distilled water, polished carefully with alumina powder having different particle size (1.0, 0.3 and 0.05 μm) to a mirror finish surface. The residual polishing material was removed by repetitive rinsing of the surface with distilled water. The modified electrode was prepared by scanning the potential of the polished GCE in a 0.1 mol L^{-1} HNO_3 solution containing 2.0×10^{-3} mol L^{-1} 4-amino-3-hydroxynaphthalene-sulfonic acid (AHNSA) between −0.8 and 2.0 V for 15 cycles. The modified electrode was then rinsed with distilled water to remove physically adsorbed and unreacted species from the electrode surface. Subsequently, the modified electrode was stabilized in 0.5 mol L^{-1} H_2SO_4 by scanning the potential between −0.8 and +0.8 V until a steady cyclic voltammogram was obtained. Finally, the modified electrode was dried in air and made ready for use.

2.3. Analytical procedure

Quantitative analyses of the caffeine content of aqueous samples were performed using square wave voltammetry. Aqueous stock solution of caffeine (10×10^{-3} mol L^{-1}) in pH 5 acetate buffer solution (ABS) was prepared, and kept in the dark under refrigeration. Acetate buffer (0.1 mol L^{-1}) solutions of various pHs were used as base solutions for the determination of caffeine. Calibration curve constructed using the peak current for the standard solutions was used to determine the caffeine content of coffee extracts. Ethiopian coffee purchased from the supermarket was roasted, ground, boiled in water and then was extracted by decantation. The organic solvent free filtrate of the coffee extract was made ready for measurement after diluting it with pH 5.0 ABS in a volume ratio of 1:200. The recovery of the method was evaluated by spiking the coffee extract with standard caffeine solutions of different concentrations. The effect of potential interferents on the determination of caffeine in coffee extract and the electrocatalytic stability of the modified electrode were also studied.

3. Results and discussion

3.1. Electropolymerization of poly(4-amino-3-hydroxynaphthalene-sulfonic acid)

Fig. 1 shows cyclic voltammograms of 2.0×10^{-3} mol L^{-1} AHNSA in 0.1 mol L^{-1} HNO_3 at the polished GCE. In the first scan, anodic peak (1), anodic peak (2) and cathodic peak (3) were observed with peak potentials +0.260 V, +0.690 V and −0.250 V, respectively. From the second cycle onwards, a new anodic peak (4) appeared at +0.110 V. Upon continuous scanning cycles, the peaks' current of all except anodic peak (2) increased reflecting the continuous growth of the film of electropolymerization. Fig. 2A depicts the cyclic voltammograms of bare GCE (curve a) and stabilized polymer-modified GCE (curve b) recorded between −0.8 and +0.8 V in pH 5 ABS monomer free solution. Appearance of three distinct redox peaks at the modified electrode (curve b) which are absent at the unmodified GCE (curve a) is conformation of the deposition of the polymer film at the GCE surface.

The effect of potential scan rate on the electrochemical behavior of the modified electrode was also investigated. Fig. 2B shows the CVs of the modified electrode in pH 5.0 ABS at different scan rates. Inset of Fig. 2B shows the linear dependence of the cathodic peak current of peak 1 (Fig. 2B) on the scan rate in the range of 20–300 mV s^{-1}. The linear dependence of the peak current on the scan rate indicates surface-confined reaction kinetics [31].

3.2. Electrochemical behavior of caffeine

The electrochemical behavior of caffeine at the polymer-modified electrode was investigated using cyclic voltammetry. Fig. 3 shows the CVs of bare GCE (curve a) and poly(AHNSA) modified GCE (curve b) in pH 5.0 ABS containing 1×10^{-3} mol L^{-1} of caffeine recorded under similar conditions. At the bare GCE, caffeine exhibited a poor and irreversible oxidative peak centered at about +1.60 V (curve a). But at the modified electrode (curve b), a well-defined, irreversible anodic peak with an enhanced peak current was observed at +1.45 V. This could be ascribed to the selective preferential accumulation of caffeine on surface bound functionalities of the polymer-modified electrode [32]. The potential shift to a lower positive potential along with current enhancement at the modified electrode relative to the unmodified electrode indicate the catalytic oxidation of caffeine at the polymer-modified electrode.

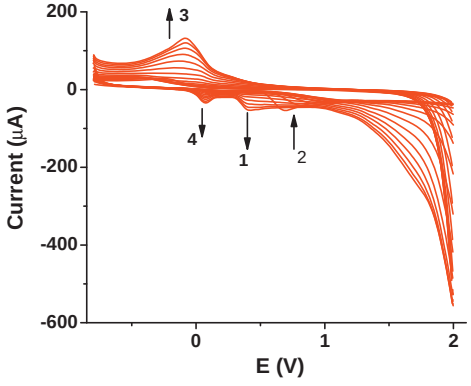


Fig. 1. Cyclic voltammograms of bare GCE in 2 mM AHNSA (0.1 mol L^{-1} HNO_3). Scanning potential: −0.8 to +2.0 V; number of segments: 30; scan rate: 0.1 V s^{-1}.

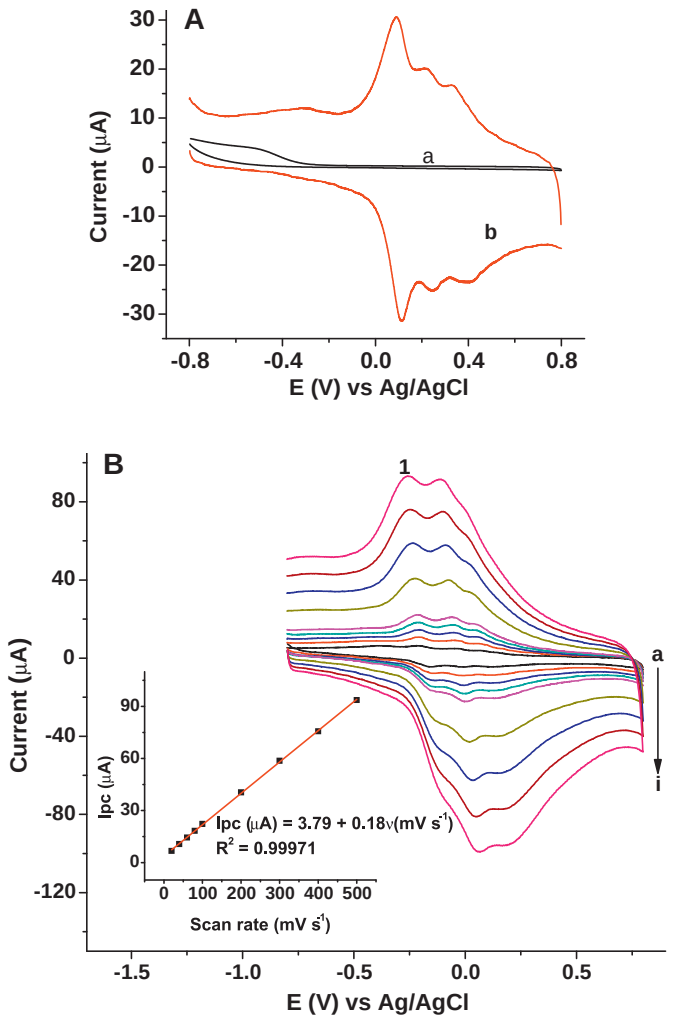


Fig. 2. (A) CVs of unmodified GCE (curve a) and stabilized poly(AHNSA)/GCE (curve b) in pH 5 ABS at a scan rate of 0.1 V s^{-1}. (B) CVs of a stabilized poly(AHNSA)/GCE in pH 5 ABS at different scan rates. Inset: plot of cathodic peak current of the modified electrode in pH 5 ABS *versus* potential scan rate (scan rate: (a–i): 20, 40, 60, 80, 100, 200, 300, 400, 500 mV s^{-1}).

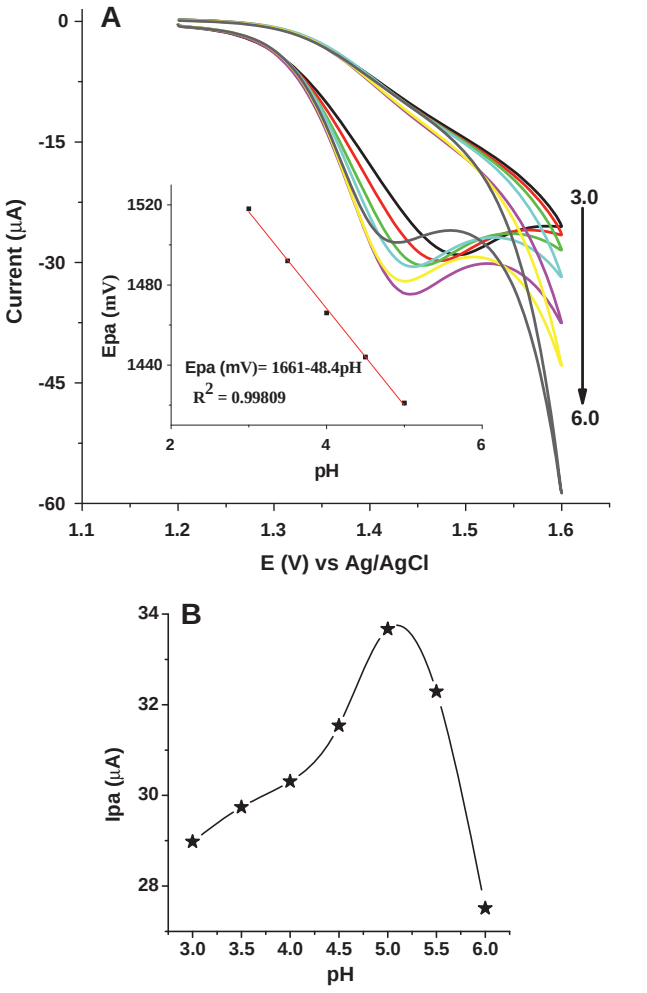


Fig. 4. (A) CVs of poly(AHNSA) modified GCE in ABS of different pHs (3.0–6.0) containing 1.0×10^{-3} mol L^{-1} of caffeine. Inset: plot of anodic peak potential *versus* pH of buffer solution. (B) Plot of *Ipa versus* pH in pH range 3.0–6.0 at a scan rate of 100 mV s^{-1}.

3.3. Effect of pH and scan rate

The effect of pH on the peak current and peak potential of caffeine was investigated in the pH range 3.0–6.0 ABS (Fig. 4A).

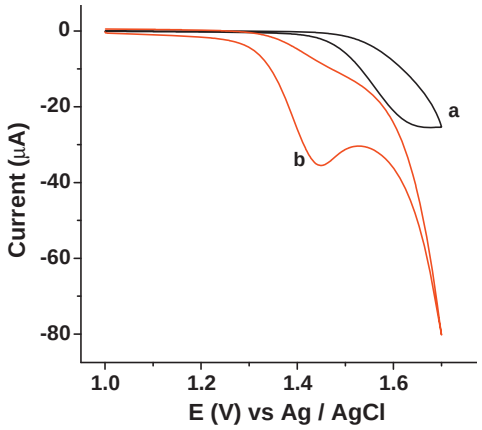


Fig. 3. Cyclic voltammograms of bare GCE (a) and poly(AHNSA)/GCE (b) in pH 5 ABS containing 1.0×10^{-3} mol L^{-1} caffeine at a scan rate of 100 mV s^{-1}.

The peak potential shifted negatively with increasing pH. Plot of peak potentials *versus* pH was found to be linear over the pH range 3.0–5.0 with a slope of 48.4/pH and correlation coefficient of $R^2 = 0.99809$ (inset of Fig. 4A), corresponding to a mechanism involving protons and electrons in a 1:1 ratio [33]. It was also observed that the peak current of caffeine at the poly(AHNSA)/GCE increased with increase in pH from 3.0 to 5.0 and then started to decrease for pH values higher than 5.0 (inset of Fig. 4B). The increase in the peak current from pH 3.0 to 5.0 could partly be ascribed to the increasing electrostatic attraction between the polymer-modified surface ($pKa \approx 4$) [34] and the positively charged caffeine (pKa 10.4) [35]. Hence, pH 5.0 was chosen as the optimum pH for further analyses.

The effect of scan rate on the oxidative peak current of 1×10^{-3} mol L^{-1} caffeine at poly(AHNSA)/GCE in pH 5 ABS was also studied. Fig. 5A shows the CVs at different scan rates in the range 20–300 mV s^{-1}. Inset of Fig. 5A depicts the linear dependence of the anodic peak current on the scan rate in the range 20–300 mV s^{-1} which indicates the reaction of caffeine at the surface of the polymer-modified electrode follows surface-confined kinetics [31]. For such an irreversible surface-confined process, the current response (*Ipa* in A), surface coverage (Γ in mol cm^{-2}),

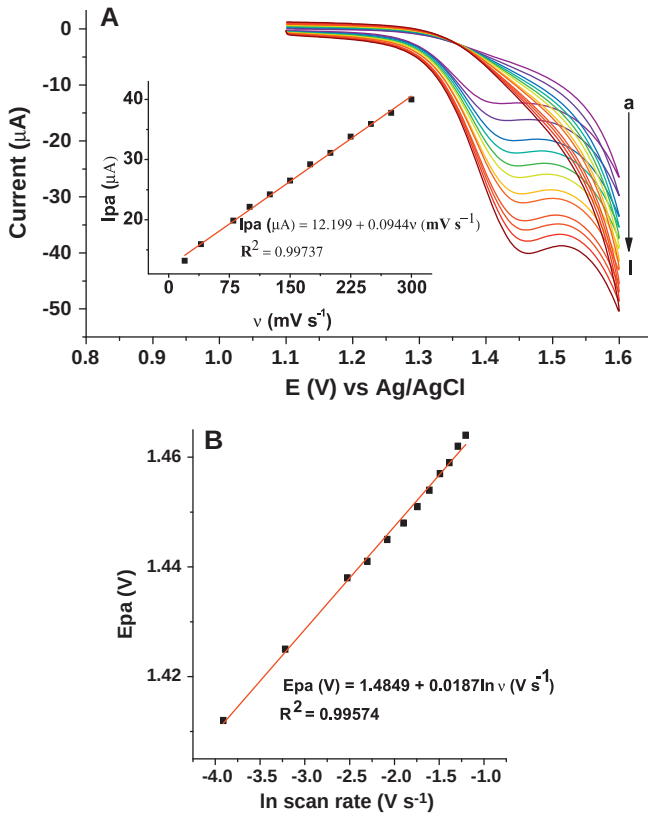


Fig. 5. (A) CVs of poly(AHNSA) modified GCE in pH 5.0 ABS containing 1.0×10^{-3} mol L^{-1} caffeine at different scan rates ((a–l): 20, 40, 80, 100, 125, 150, 175, 200, 225, 250, 275 and 300 mV s^{-1}, respectively). Inset: plot of anodic peak current of 1.0×10^{-3} mol L^{-1} caffeine *versus* scan rate. (B) Plot of peak potential *versus* ln(ν).

number of electrons involved (n) and the charge consumed (Q in coulombs) are related by Eqs. (1)–(3) [36]:

$$Ipa = \frac{n^2F^2}{4RT}\nu A\Gamma \quad (1)$$

$$n = \frac{4Ipa\ RT}{FQ\nu} \quad (2)$$

$$\Gamma = \frac{Q}{nFA} \quad (3)$$

where F is the Faraday's constant, R is the gas constant, T is the temperature (K), A is the electrode area (cm^2) and ν is the scan rate (V s^{-1}). Integrating the anodic peak of 1×10^{-3} mol L^{-1} caffeine at 0.1 V s^{-1} scan rate and applying the above equations, the number of electrons involved and the surface coverage of caffeine at the electrode surface were calculated to be 3.8 (≈4) and

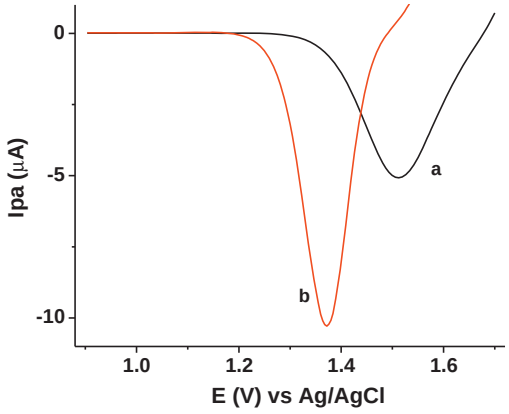


Fig. 6. SWVs of (a) bare GCE and (b) poly (AHNSA)/GCE in 1.0×10^{-3} mol L^{-1} caffeine (pH 5.0 ABS). Amplitude: 50 mV; potential step: 4 mV; frequency: 15 Hz; scanning potential: +0.9 to +1.7 V.

2.02×10^{-10} mol cm^{-2}, respectively. For such an adsorption irreversible process, the peak potential (Epa) and $ln\ \nu$ obey Eq. (4) [37]:

$$Epa\,(V) = A + \frac{RT}{(1-\alpha)nF}\ln\ \nu \quad (4)$$

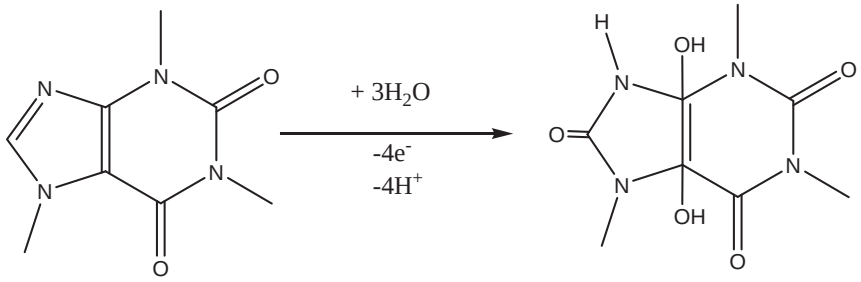
where A is a constant, which is related to the formal electrode potential (E^0) and the standard rate constant (ks) at E^0. Based on the slope of the fitted linear relationship (Fig. 5B): $Epa = 1.4849 + 0.0187\ln\nu$ (Epa: V; ν: V s^{-1}), the value of the electron-transfer coefficient (α) for the irreversible oxidation reaction of caffeine at the polymer-modified electrode is estimated to be 0.83 conforming the irreversibility of the oxidation of caffeine at the modified electrode.

From the CV responses of the polymer-modified electrode for caffeine (Fig. 3), the effect of pH on the peak potential (inset of Fig. 4A) and calculated value of n, the proposed reaction mechanism is shown in Scheme 2 which is in agreement with the mechanism reported elsewhere [21].

Since square wave voltammetry (SWV) has a much higher sensitivity and better resolution than cyclic voltammetry [38], the applicability of the poly(AHNSA) modified GCE for the quantitative determination of caffeine has been investigated by SWV. The polymer-modified GCE (Fig. 6b) enhanced the current response for caffeine by 2 folds as compared to the bare GCE (Fig. 6a) in addition to shifting the potential in the positive direction by 144 mV. These effects are clear conformation for the catalytic effect of the polymer film.

3.4. Effect of accumulation potential and time

Fig. 7 depicts the effect of accumulation potential and accumulation time on peak current response of poly(AHNSA)/GCE for caffeine. The peak current increased with increasing E_{acc} from



Scheme 2. Proposed reaction mechanism of caffeine at poly(AHNSA) modified GCE.

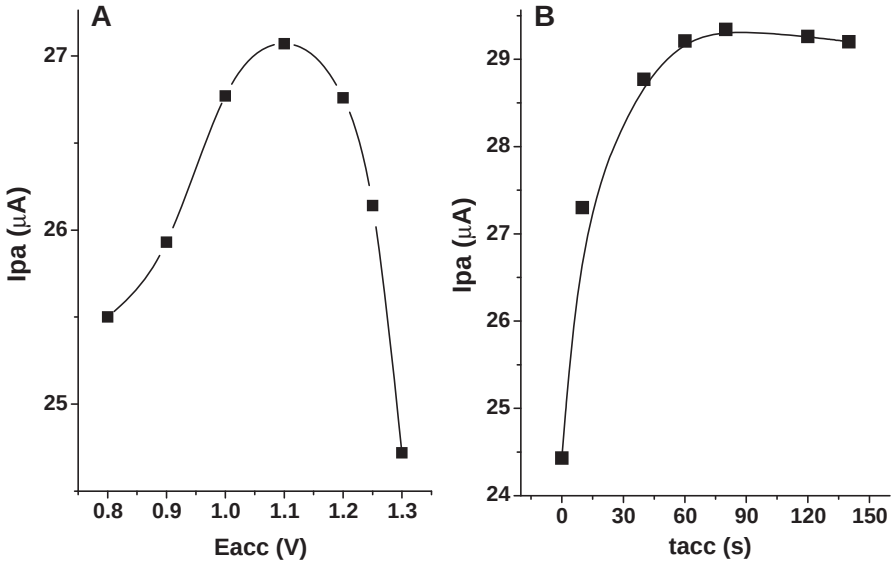


Fig. 7. Anodic peak current response of poly(AHNSA) in 1.0×10^{-3} mol L^{-1} caffeine (pH 5.0 ABS) at (A) different accumulation potentials (+0.8 to +1.3 V) and 30 s of accumulation time and (B) different accumulation time (0–140 s) and +1.1 V of accumulation potential.

+0.8 to +1.1 and then dropped at higher potentials (Fig. 7A). The observed decrease in the current response at potentials higher than +1.1 could be because; the applied potential is high enough to cause the oxidation of caffeine than to accumulate it at the surface of the electrode. Fig. 7B shows the effect of t_{acc} recorded at E_{acc} of +1.1 V. The current response increased gradually up to 80 s and then leveled off which could probably be due to saturation of the electrode surface. Thus, E_{acc} of +1.1 V and t_{acc} of 80 s were taken as the optimum preconcentration potential and time, respectively.

After the optimization of the solution pH and preconcentration conditions, the SWV parameters (pulse amplitude, potential step and frequency) were optimized to be 70 mV, 14 mV and 30 Hz, respectively and were used in the subsequent analyses.

3.5. Calibration curve and detection limit of caffeine at poly(AHNSA)/GCE

Using the optimized conditions described above, the anodic peak currents at +1.340 V were found to be proportional to caffeine concentration in the range 6.0×10^{-8} to 4.0×10^{-5} mol L^{-1} (Fig. 8) with a linear regression equation, correlation coefficient and detection limit of *Ipa* (μA) = 0.289 + 0.503 *C* (10^{-6} mol L^{-1}), $R^2 = 0.99872$ (inset of Fig. 8) and 6.7×10^{-8} mol L^{-1} (S/N = 3), respectively. When the concentration of caffeine was more than 4.0×10^{-5} mol L^{-1}, the current response decreased gradually which could be ascribed to the saturation of the active sites of the polymer film.

3.6. Application of the method for the determination of caffeine in coffee

The SWV method developed was applied for the determination of caffeine in coffee extracts. Coffee extract samples were prepared as described in the procedure. Using the optimized conditions, square wave voltammograms of caffeine in coffee extract were recorded (curve a of Fig. 9A). The average result of three separate determinations of caffeine in coffee extract samples at 95% confidence level, was 67.2 ± 0.095 mg/100 mL which is in the range reported in the literature [5,6]. Furthermore, three equal volumes of coffee extract samples in pH 5.0 ABS (1:200 diluted) were spiked with different concentrations of standard caffeine (4, 6 and 8 μM) and the square wave voltammograms were recorded (curves b–d in Fig. 9A). The current response, percentage recoveries and percentage standard errors are summarized in Table 1. The method showed excellent recoveries signifying the potential applicability of poly(AHNSA)/GCE for the determination of caffeine in real samples such as coffee without any interferences from sample matrices.

The possible interference from compounds of similar structures in the determination of caffeine was further studied. Fig. 9B shows the SWVs of variable concentrations of caffeine (4, 6, 10, 20 and 40 μM caffeine) in the presence of constant concentration of theophylline (10 μM); which is one of the N-methyl derivatives of xanthine [12]. Clearly, there is an increase in the voltammetric peak current corresponding to oxidation of caffeine with the increase of the concentration whereas the peak current response for theophylline almost remaining constant. This confirms that analysis of caffeine in coffee extract using the polymer-modified electrode is not affected not only by the sample matrices but also by structurally similar compounds like theophylline.

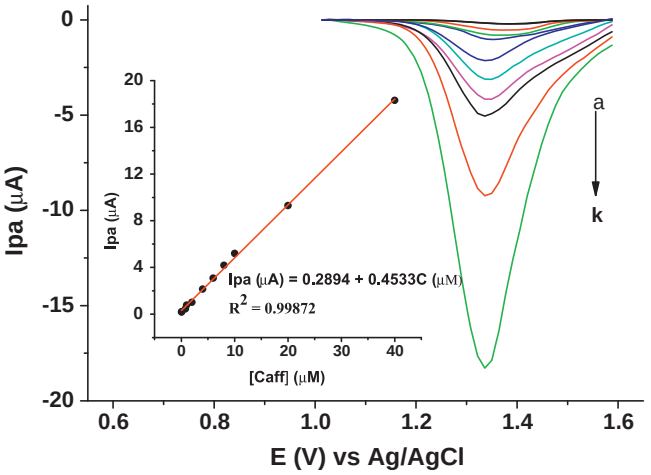


Fig. 8. SWVs of poly(AHNSA) in pH 5.0 ABS containing caffeine of different concentrations ((a–k): 0.06, 0.08, 0.8), 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 20.0 and 40.0 μM, respectively). Inset: plot of anodic peak current *versus* concentration of caffeine.

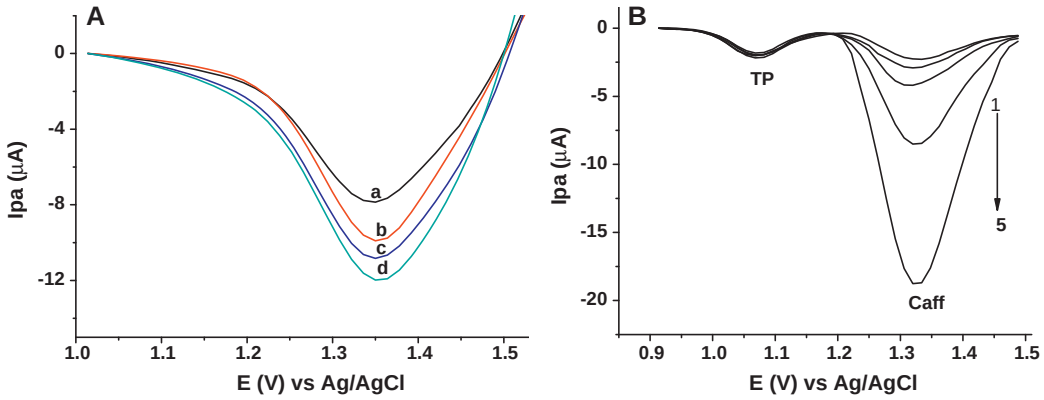


Fig. 9. (A) SWVs of poly(AHNSA)/GCE in coffee extracts (200 times diluted with pH 5 ABS) spiked with standard caffeine of different concentrations ((a–d): 0, 4, 6 and 8×10^{-6} mol L^{-1}, respectively). (B) SWVs of variable concentrations of standard caffeine in pH 5 ABS containing constant concentration of theophylline (10×10^{-6} mol L^{-1}). Concentration of standard caffeine (1–5) 4, 6, 10, 20, 40×10^{-6} mol L^{-1}, respectively.

Table 1
Percentage recoveries of spiked standard caffeine in coffee extract.

Sample	Initial (μM)	Spiked (μM)	Detected[a] (μM)	Recovery[a] (%)
Coffee extract	17.35	4.0	21.10 ± 0.115	93.75 ± 2.32
Coffee extract	17.35	6.0	23.00 ± 0.127	94.17 ± 2.11
Coffee extract	17.35	8.0	25.41 ± 0.386	100.75 ± 3.32

[a] Mean of triplicate measurements.

Table 2
Comparison between the newly developed method and other reported methods.

Electrode	Method	Linear range (mol L^{-1})	LoD (mol L^{-1})	Ref. no.
Sarfactant/MWCNTs	AdSDPV	2.91×10^{-7} to 6.27×10^{-5}	8.83×10^{-8}	[21]
Nafion/GCE	DPV	9.95×10^{-7} to 1.06×10^{-5}	7.98×10^{-7}	[22]
Nafion/MWCNTs/GCE	DPV	6×10^{-7} to 4×10^{-4}	2.3×10^{-7}	[23]
MWCNTs/Nafion/GCE	DPSV	2.9×10^{-6} to 3.77×10^{-4}	5.13×10^{-7}	[24]
MIP	SWV	6×10^{-8} to 2.5×10^{-5}	1.5×10^{-8}	[26]
Nafion/boron-doped diamond electrode	DPV	2×10^{-7} to 1.2×10^{-5}	1.0×10^{-7}	[27]
Boron-doped diamond	DPV	9.7×10^{-6} to 1.1×10^{-4}	7.0×10^{-6}	[28]
Poly(safranine)/GCE	LSV	3×10^{-7} to 1×10^{-4}	1.0×10^{-7}	[29]
Poly(AHNSA)/GCE	SWV	6×10^{-8} to 4×10^{-5}	6.7×10^{-8}	This work

3.7. Stability and comparison of the method developed with other similar methods

The stability of poly(AHNSA)/GC electrode towards caffeine oxidation was tested *via* the retention of the electrocatalytic currents (i/i_0, where i_0 represents the current recorded during the first cycle and i during successive cycles) [39] as a function of the number of cycles. The modified electrode was first scanned repetitively in the supporting electrolyte until a steady current was attained. Then, the stabilized electrode was put in pH 5 ABS containing 1×10^{-3} mol L^{-1} caffeine. Two SWV measurements were recorded daily at an interval of 8 h for ten consecutive days. To secure the cleanness of the electrode, each measurement was preceded by linear scanning of the electrode in pH 5.0 ABS in the negative direction of the same potential window. The calculated mean current ratio (i/i_0) for twenty measurements in ten days duration was 0.99958 ± 0.00437 demonstrating the stability of the electrode.

The method developed is compared with other similar electroanalytical methods (Table 2). Apart from the stability and simplicity in the preparation of the modified electrode, the present method gives a reasonably lower detection limit and wider linear range.

4. Conclusion

The approach taken in this work provides a simple method for the determination of caffeine in coffee samples. The modifier is relatively cheaper than other modifiers reported and easily deposited at the electrode surface. A wide linear response up to 6.0×10^{-8} mol L^{-1} and a limit of detection as low as 6.7×10^{-8} mol L^{-1} was observed. Excellent recoveries with acceptable errors were achieved for the determination of spiked standard caffeine samples in coffee extracts. Therefore, the method developed can be used for the direct analysis of caffeine content in real samples.

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