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Electroanalytical Determination of Gemifloxacin Mesylate in Bulk, Tablets and Human Urine Using Gold Nanoparticles Modified Carbon Paste Electrode

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A simple, precise, inexpensive and sensitive voltammetric method has been developed for the determination of gemifloxacin mesylate (GEM) in the presence of tween 80 in the bulk, farmaceutical dosage forms and human urine at gold nanoparticles modified carbon paste electrode (GNCPE). The electrochemical behavior of GEM has been investigated by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The electrochemical oxidation of GEM was an irreversible process which exhibited adsorption-diffusion controlled process behavior in Britton-Robinson (BR) buffer over the entire pH range of values from 2 to 9. The adsorptive stripping response was evaluated as a function of some variables such as pH, type of surfactant, scan rate and accumulation time. The anodic peak current varied linearly over the range from 8.0×10^{-7} to 2.8×10^{-5} M. The limits of detection and quantification were 7.32×10^{-8} M and 2.44×10^{-7} M, respectively. The relative standard deviations and the percentage recoveries were found in the following ranges: 0.58-1.35% and 99.37-101.76%, respectively.

Keywords: Gemifloxacin, Gold nanoparticles, Voltammetry, Tween 80, Urine

INTRODUCTION

Gemifloxacin mesylate (GEM) is a fluoroquinolone antibacterial agent which has an enhanced affinity for topoisomerase IV. GEM has a broad spectrum of activity against Gram-positive and Gram-negative bacteria and is being developed for the treatment of respiratory and urinary tract infections [1,2]. The chemical structure of GEM is shown in Fig. 1.

Due to its clinical advantages, GEM is receiving a great interest and there was an increase in number of its pharmaceutical dosage forms in the market in recent past. For routine analysis of the studied drugs, a simple, rapid and cost effective analytical method was required.

No official pharmacopoeial method has been found for the assay of GEM in its pharmaceutical formulations. Several methods have been reported for the determination of GEM either in pure form, dosage form, or biological fluids like chromatography [3-13], spectrophotometry [13-26], capillary electrophoresis [27,28], spectrofluorimetry [29,30], voltammetry [31-33] and potentiometry [34].

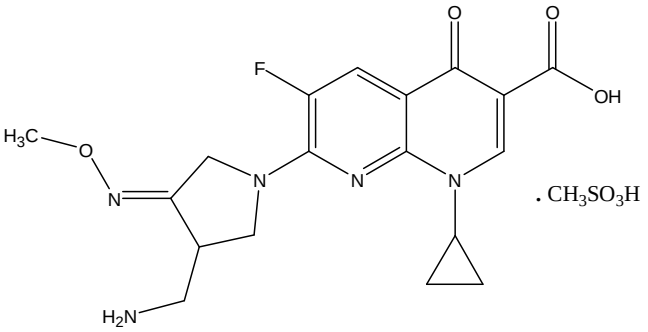

Fig. 1. Chemical structure of GEM.

Electrochemical studies have shown some properties for Gold nanoparticles (GNPs) like improving the electrode conductivity and surface area enhancement, facilitating the

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electron transfer and electrocatalytic activity, which makes it a promising candidate for electrode modification [35-40].

EXPERIMENTAL

Reagent and Solutions

The active ingredient pharmaceutical drug GEM and its dosage form, Gemiloxes tablets, containing 320 mg GEM per tablet, manufactured by Sabaa International Company for Pharmaceuticals & Chemical Industries, Egypt.

Stock solutions of 1×10^{-3} M of GEM was prepared by dissolving a calculated weight of the active ingredient drug in deionized water. More dilute solutions were prepared daily just before the use. Ascorbic acid (AA), uric acid (UA), sodium dodecyl sulphate (SDS), tween 80 and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. Britton-Robinson (BR) buffer solutions (pH 2-9) were used as supporting electrolytes. BR buffers were made in a usual way (*i.e.* by mixing a solution of 0.04 M phosphoric acid, 0.04 M acetic acid and 0.04 M boric acid). Buffer solutions were adjusted by adding the necessary amount of 2.0 M NaOH solutions to obtain the appropriate pH. Graphite powder, paraffin oil and hydrogen tetrachloroaurate were supplied from Sigma-Aldrich. All solutions were prepared from pure analytical grade chemicals.

Construction of Gold Nanoparticles Modified Carbon Paste Electrode

Carbon paste electrode (CPE) was prepared by mixing 0.5 g graphite powder and 0.3 ml paraffin oil in a mortar with a pestle to obtain the carbon paste, then the paste was packed into the hole of the electrode body and smoothed on a filter paper until it had a shiny appearance, then CPE was immersed into a 6 mM hydrogen tetrachloroaurate ($HAuCl_4$) solution containing 0.1 M KNO_3 prepared in doubly distilled water and deaerated by bubbling with nitrogen. A constant potential of -0.4 V was applied for 400 s versus Ag/AgCl reference electrode. The obtained gold nanoparticles modified carbon paste electrode (GNCPE) was washed with doubly distilled water and dried carefully before being used [41].

Electrochemical Measurements

All voltammetric measurements were performed using a pc-controlled AEW2 electrochemistry work station, and data were analyzed with ECprog3 electrochemistry software, manufactured by Sycopel Scientific Limited (Tyne & Wear, UK). The one compartment glass cell with the three electrodes was connected to the electrochemical workstation through a C-3-stand from BAS (USA). A platinum wire from BAS (USA) was employed as auxiliary electrode. All the cell potentials were measured with respect to Ag/AgCl (3 M NaCl) reference electrode from BAS (USA). Solutions were degassed using pure nitrogen prior and throughout the electrochemical measurements. A JENWAY 3510 pH meter (England) with glass combination electrode was used for pH measurements. Scanning electron microscopy SEM measurements were carried out using a JSM-6700F scanning electron microscope (Japan Electro Company). All the electrochemical experiments were performed at an ambient temperature of 25 ± 0.2 ºC.

Effect of Surfactants

The cyclic voltammetric technique of 1×10^{-3} M GEM (in BR buffer, pH 2.0) was studied on GNCPE upon successive additions of 1×10^{-2} M SDS solution to the electrolytic cell and the voltammograms were recorded using CV. The experiments were repeated by using tween 80 and CTAB at the same concentration of SDS.

Determination of GEM in Bulk Powder

Aliquots of GEM solution (1×10^{-3} M) were added to the electrolytic cell containing 5 ml of BR buffer of pH 2. The solution was stirred for 5 s at open circuit conditions in the presence of 50 µl of tween 80 (1×10^{-2} M) at GNCPE and voltammetric analyses were carried out and the voltammograms were recorded at scan rate = 10 mV s^{-1}, pulse width = 25 ms and pulse amplitude = 50 mV.

Determination of GEM in Tablets

Ten tablets were weighed and the average mass of per tablet was determined. A portion of the finely grounded material needed to prepare 1×10^{-3} M GEM solution was transferred into the 100 ml calibrated flask containing 70 ml of deionized water. The content of the flask was sonicated for about 20 min and then made up to the volume with deionized water. The solution was filtered to separate the insoluble excipients. Aliquots of the drug solution were

introduced into the electrolytic cell and the voltammograms were recorded.

Analysis of GEM in Urine

For the determination of GEM in spiked urine, urine (1.0 ml) was mixed with 9 ml of BR buffer of pH 2. Successive additions of 1×10^{-3} M GEM were added to the voltammetric cell 5 ml of the previously diluted urine and the voltammograms were recorded using DPV.

RESULTS AND DISCUSSION

Electrochemical Behavior of GEM and Effect of pH

Figure 2A shows the electrochemical behavior of 1×10^{-3} M GEM in BR buffer at different pH values from 2 to 9 at CPE exhibiting an anodic peak, with no peak on the reverse scan over the entire pH range, suggesting the irreversible nature of the electrode reaction. It is concluded from the figure that a well-defined anodic peak of maximum

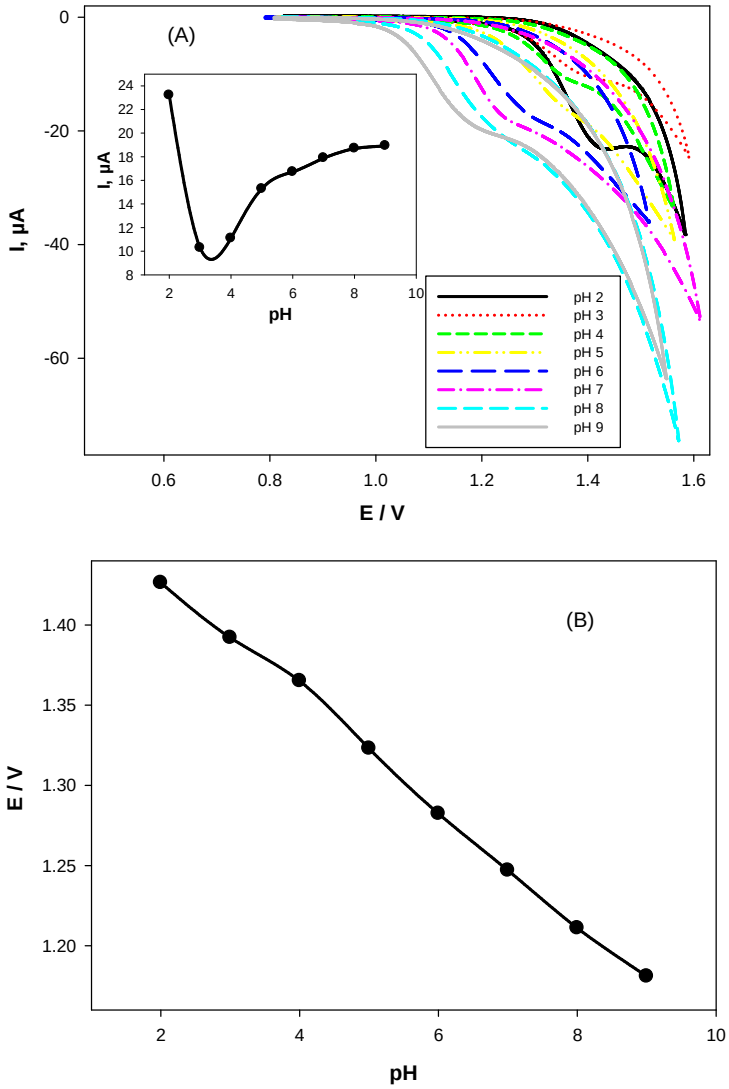

Fig. 2. Cyclic voltammograms of the effect of solution pH on the oxidation of GEM (1×10^{-3} M) at CPE using BR buffer at scan rate of 100 mV s^{-1} (A). The inset: plot of anodic peak currents as a function of pH (A) and plot of E-pH for GEM at CPE (B).

current value is obtained at pH 2.0. According to Fig. 2, after pH 3 the anodic current increases by increasing pH. Therefore, pH 2.0 was chosen as the optimum pH value for determination of GEM. Figure 2B shows that the anodic peak potential (E) has shifted negatively with the increase of the solution pH indicating that the oxidation of GEM at GNCPE is pH dependent reaction and that protons have taken part in their electrode reaction processes.

Effect of Surfactants

Figure 3 shows the comparison between successive additions of different surfactants such as SDS, tween 80 and CTAB of the same concentration (1×10^{-2} M) to 1×10^{-3} M GEM in BR buffer of pH 2. The maximum anodic peak current values of 28.2, 31.1 and 27 µA were found at concentrations of 8×10^{-5} M, 1×10^{-4} M and 4×10^{-5} M in case of SDS, tween 80 and CTAB, respectively. Therefore,

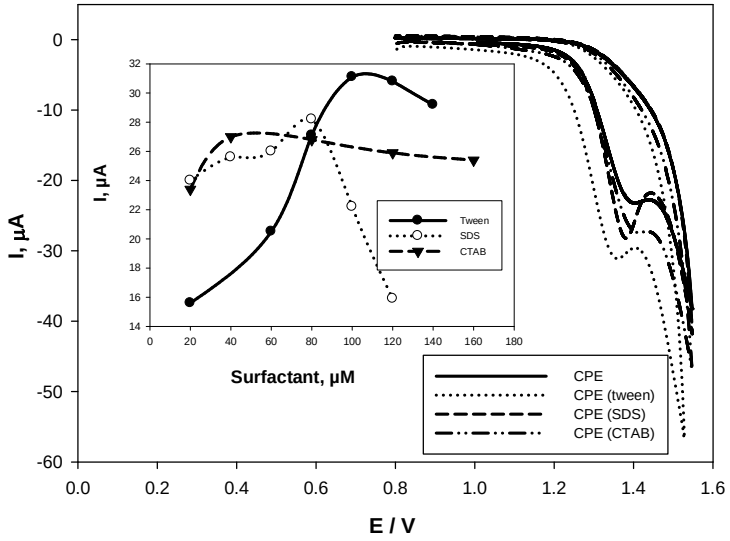

Fig. 3. Cyclic voltammograms of the effect of surfactants concentration: SDS, tween 80 and CTAB on GEM (1×10^{-3} M in BR buffer of pH 2) at CPE at scan rate of 100 mV s^{-1}. The inset: plot of the anodic peak current as a function of surfactants concentration.

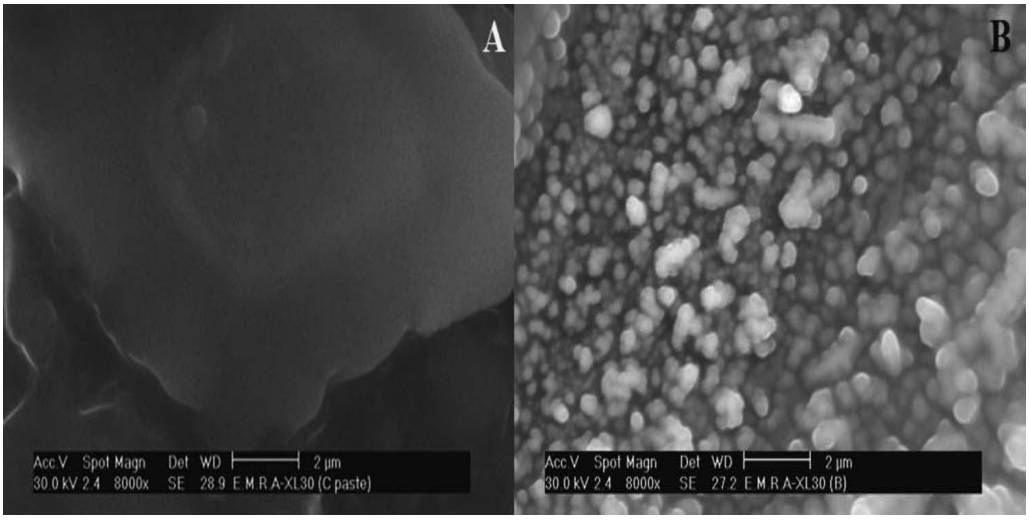

Fig. 4. SEM of (A) CPE and (B) GNCPE.

the maximum current of GEM was found in the presence of 1×10^{-4} M of tween 80.

Morphologies of Different Electrodes

The response of an electrochemical sensor is related to its physical morphology, as shown in Fig. 4. The SEM of CPE and GNCPE are given elsewhere [41]. Significant differences are observed in the surface structure of the two electrodes. For CPE, isolated and irregularly shaped graphite flakes and separated layers are noticed. In the case of GNCPE surface, the metallic nanoparticles are located at different elevations. Moreover, a random distribution and interstices among the nanoparticles were observed in SEM image of the GNCPE producing large surface area.

Electrochemistry of GEM at GNCPE

Figure 5 shows typical cyclic voltammograms of 1×10^{-3} M GEM in BR buffer of pH 2 at scan rate 100 mV s^{-1} recorded at different working electrodes in absence and in the presence of 1×10^{-4} M^1 tween 80 (*i.e.* CPE (solid line), CPE/tween 80 (dotted line), GNCPE (short dashed line) and GNCPE/tween 80 (long dashed lines) electrodes, respectively). At CPE, the oxidation peak was observed with current response 21.97 μA, whereas at CPE/tween 80, the current (I) response increases to 30.42 μA. At GNCPE the current response increases to 41.39 μA. Whereas, at GNCPE/tween 80 the current response increases to 73.22 μA suggesting that GNCPE/tween 80 can be used to improve the determining sensitivity of GEM.

Effect of Scan Rate

The effect of different scan rates (ν ranging from 10 to 250 mV s^{-1}) on the oxidation current response of 1×10^{-3} M GEM at GNCPE/tween 80 in BR buffer (pH 2) was studied and CV curves of GEM at different scan rates are shown in Fig. 6. The peak potential also increases as the scan rate increases. A linear relationship is found for the logarithm of the oxidation peak currents and the logarithm of the scan rates (Fig. 6 inset). The oxidation peak currents increase linearly with the linear regression equations as $\log I = 0.144 + 0.87 \log \nu$, with a correlation coefficient of 0.998. The slope 0.87 suggests that the oxidation reaction at the electrode surface takes place under adsorption-diffusion controlled process [42,43].

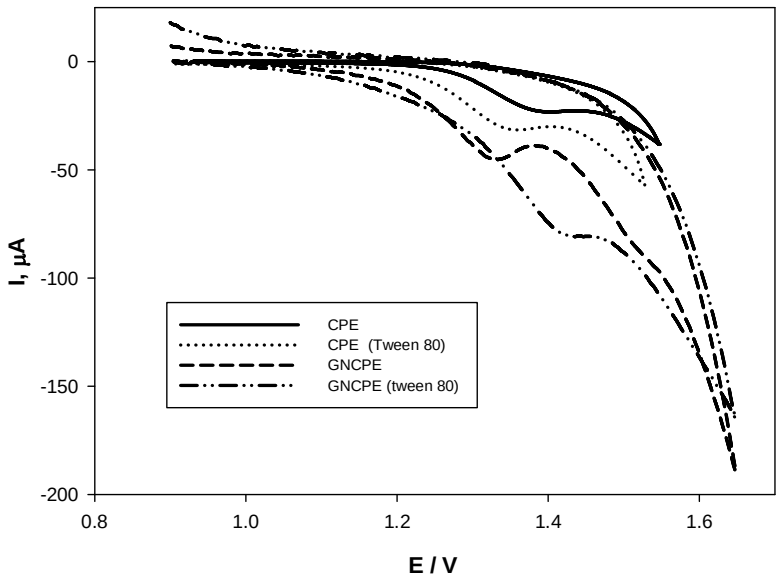

Fig. 5. Cyclic voltammograms of 1×10^{-3} M GEM in BR buffer of pH 2 at scan rate of 100 mV s^{-1} recorded at 1) CPE (——), 2) CPE/tween 80 (…..), 3) GNCPE (- - - - -) and 4) GNCPE/tween 80 (—.—.—).

Effect of Accumulation Time

Figure 7 shows the dependence of the adsorptive peak current on the accumulation time (T_{acc}) of 1×10^{-3} M GEM at GNCPE/tween 80. Sharp increasing in the current value was obtained at 5 s. Thus, considerable increase in sensitivity can be achieved by the application of adsorptive-stripping voltammetry to determine GEM. It was found that peak current reached to its maximum value at T_{acc} of 5 s, but then decreased with increasing time. Therefore, the preconcentration time of 5 s was chosen as the optimum accumulation time for the determination of GEM.

Effect of Interferences of Ascorbic Acid (AA) and Uric Acid (UA)

An important parameter for a sensor is its ability to discriminate between the interfering species commonly

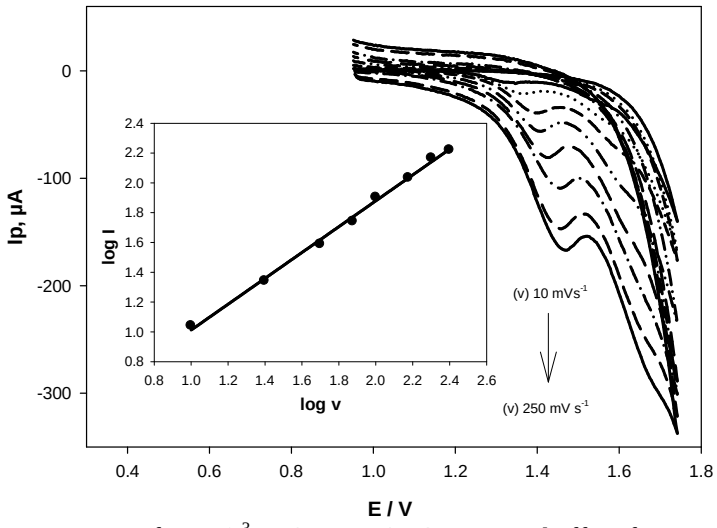

Fig. 6. Cyclic voltammograms of 1×10^{-3} M GEM at GNCPE in BR buffer of pH 2 at: 10, 25, 50, 75, 100, 150, 200 and 250 mV s^{-1}, 1×10^{-4} M tween 80. The inset: plot of logI values *vs*. log*v*.

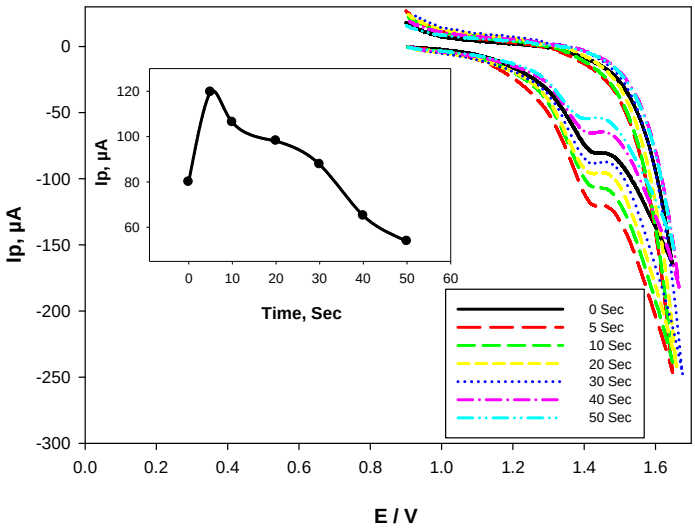

Fig. 7. Cyclic voltammograms of 1×10^{-3} M GEM at GNCPE in BR buffer of pH 2 as a function of accumulation Time from 0.0 to 50 s at scan rate of 100 mV s^{-1}, 1×10^{-4} M tween 80. The inset: plot of the anodic peak current values *vs*. accumulation time.

present in similar physiological environment and the target analyte. AA is a naturally occurring organic compound with antioxidant properties. Humans require it as part of their nutrition [44]. UA is the primary end product of purine metabolism in the human body [45]. Extreme abnormalities of UA levels are symptomatic of several diseases, including gout, hyperuricemia and Lesch-Nyan disease [46]. Therefore, determination of GEM in the presence of AA and UA is very important for the clinical point of view.

DPV was used to determine GEM in the presence of the equimolar solutions (1×10^{-4} M) of AA and UA in BR buffer (pH 2); the applied scan rate was 10 mV s^{-1}. Figure 8 (curves A and B) shows the differential pulse voltammograms obtained by the mixtures of GEM/AA and GEM/UA, respectively, at GNCPE/tween 80 with good peak separation as broad peaks for AA and UA, almost in the same potential range and sharp peak for GEM. Therefore Fig. 8 (Curve C) shows the voltammogram of the mixture of GEM, AA and UA as one broad peak for AA and UA, because AA or UA appears in the same potential range and well separated peak for GEM.

Determination of GEM

The calibration plot was given in the inset of Fig. 9 over the concentration range of 8.0×10^{-7} and 2.8×10^{-5} M with correlation coefficient of 0.9998. The limit of detection (LOD) and the limit of quantification (LOQ) were found to be 7.32×10^{-8} M and 2.44×10^{-7} M, respectively. The relative standard deviations and the percentage recoveries were found in the following ranges: 0.58-1.35% and 99.37-101.76%, respectively.

The repeatability of the proposed DPV procedure was investigated on the basis of five measurements of 3.2×10^{-6} M GEM solution, the relative standard deviation (RSD) was found to be 1.68% indicating good results.

Table 1 shows a comparison of several methods mentioned in literature for the determination of GEM. The proposed DPV method is more sensitive compared to the other reported methods.

Assay of GEM in Tablets

Standard addition method was successfully applied to the direct determination of GEM in Gemiloxes tablets using

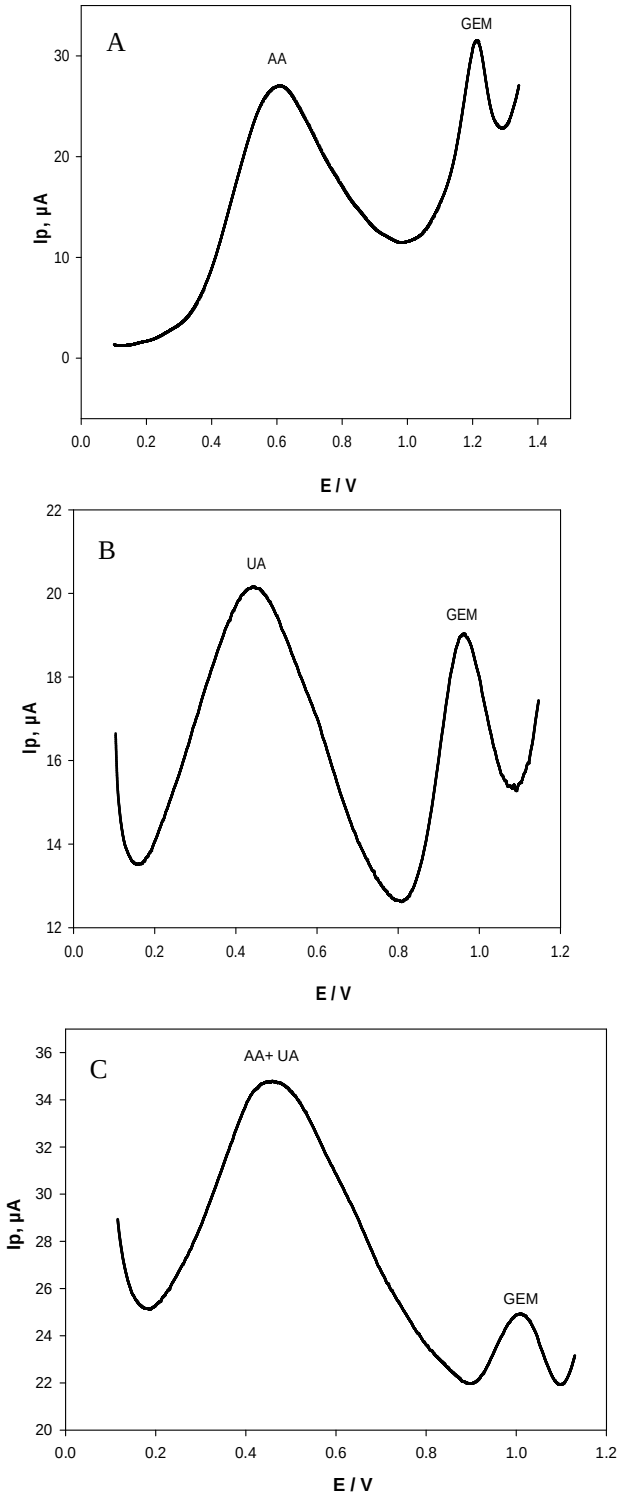

Fig. 8. Differential pulse voltammograms of (A) GEM/AA mixture, (B) GEM/UA mixture and (C) GEM/AA, UA mixture in BR buffer of pH 2 at GNCPE at scan rate of 10 mV s^{-1} in presence of 1×10^{-4} M tween 80.

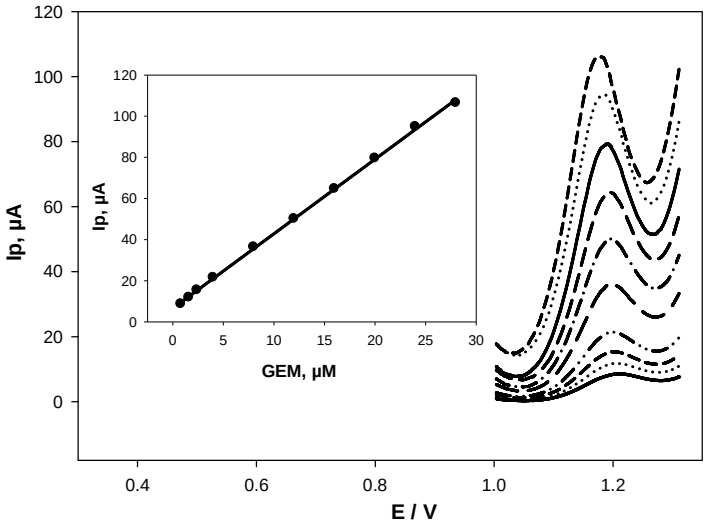

Fig. 9. Effect of changing the concentration of GEM, using DPV mode at GNCPE in BR buffer pH 2 and scan rate 10 mV s^{-1} in presence of 1×10^{-4} M tween 80. The inset: plot of the oxidation peak current *vs.* the concentration of GEM.

Table 1. Comparison of the Mentioned Methods for the Determination of GEM

Method	Linear range (M)	Ref.
	6.18×10^{-6}-3.09×10^{-5}	[18]
	2.06×10^{-5}-1.03×10^{-4}	[15]
	4.12×10^{-6}-2.06×10^{-5}	[16]
Spectrophotomery	1.05×10^{-5}-5.27×10^{-5}	[17]
	8.24×10^{-6}-2.88×10^{-5}	[13]
	2.06×10^{-5}-1.44×10^{-4}	[21]
	1.03×10^{-6}-1.03×10^{-5}	[25]
Potentiometry	1.00×10^{-5}-1.00×10^{-2}	[34]
	1.03×10^{-6}-2.06×10^{-5}	[5]
Chromatography	1.29×10^{-6}-5.15×10^{-5}	[8]
	1.03×10^{-6}-3.09×10^{-5}	[13]
The proposed DPV method	8.00×10^{-7}-2.80×10^{-5}	

GNCPE/tween 80 without the necessity for the sample pretreatment or time consuming extraction steps prior to the analysis. Based on the average of five replicate measurements, the values of mean recovery and mean RSD were 100.80% and 1.85, respectively. The obtained results in Table 2 were in acceptable limits.

Table 3 shows a comparison of several methods mentioned in literature for the determination of GEM in dosage forms. The proposed DPV method is more sensitive compared to the other reported methods.

Validation Method in Urine

Successive additions of 1×10^{-3} M GEM were added to the voltammetric cell containing 5 ml of the previously

Table 2. Determination of GEM in Gemiloxes Tablets

Gemiloxes Tablets	GEM (μM) taken	GEM (μM) added	Recovery (%)
320 mg GEM/tab	4.0	8.00	100.87
		12.0	101.45
		16.0	101.23
		20.0	99.65
Mean recovery ± RSD*			100.80 ± 1.85

*Four different concentration of GEM; number of replicates (n) = 5.

Table 3. Comparison of the Mentioned Methods for the Determination of GEM in Tablets

Method	Linear range (M)	Ref.
Spectrophotomery	1.23×10^{-5}-6.17×10^{-5}	[14]
	1.03×10^{-6}-6.18×10^{-5}	[19]
	1.647×10^{-5}-8.24×10^{-5}	[20]
	4.12×10^{-6}-1.85×10^{-5}	[22]
	2.06×10^{-5}-1.23×10^{-4}	[23]
Capillary electrophoresis	1.03×10^{-5}-1.03×10^{-4}	[28]
Chromatography	12.0×10^{-5}-6.18×10^{-5}	[10]
Voltammetry	5.08×10^{-6}-3.19×10^{-5}	[31]
The proposed DPV method	8.00×10^{-7}-2.80×10^{-5}	

diluted urine and the voltammograms were recorded at the scan rate of 10 mV s^{-1} using DPV at GNCPE/tween 80. The calibration curve (Fig. 10) gave a straight line in the range from 1.2×10^{-6} M to 2.2×10^{-5} M with correlation coefficient (R^2) = 0.9997, the LOD and LOQ were found to be 9.14×10^{-8} M and 3.05×10^{-7} M, respectively. The relative standard deviations and the percentage recoveries were found in the following ranges: 0.73-1.58% and 99.17-101.93%, respectively.

CONCLUSIONS

In the present work, gold nanoparticles modified carbon paste electrode in the presence of tween 80 was used for electrochemical determination of GEM. The advantage of the gold nanoparticles/tween 80 is the significant enhancement of the CPE sensitivity. The experimental conditions such as pH, scan rate and accumulation time were optimized to find the highest sensitivity for the

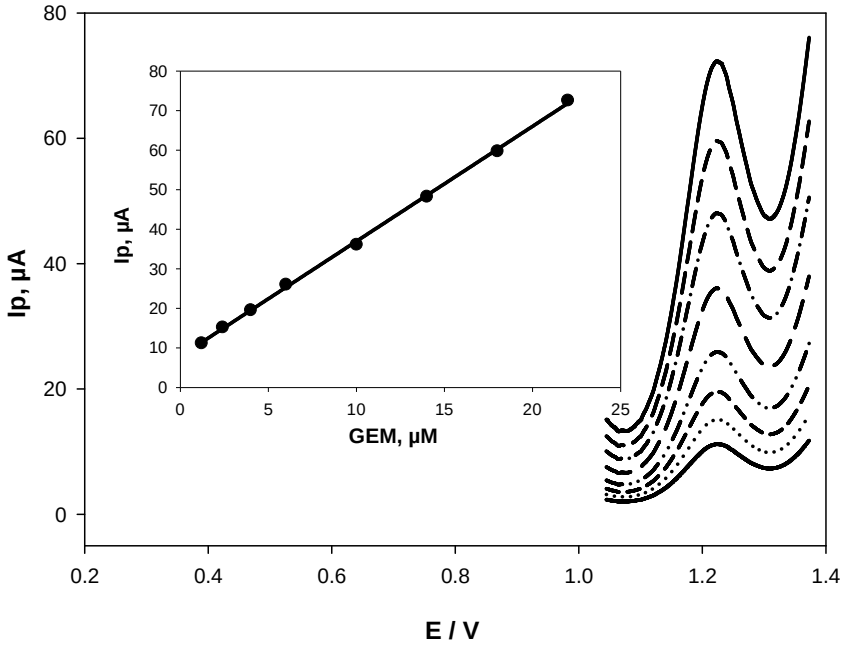

Fig. 10. Qantitative assay of GEM in urine using BR buffer pH 2, scan rate 10 mV s^{-1}, in presence of 1×10^{-4} M tween 80. The inset: plot of peak current *vs*. the concentration of GEM in urine.

determination of GEM with good precision, accuracy and low detection limit. The results showed that the method was simple and sensitive enough for the determination of GEM in clinical preparations (human urine).

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