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Voltammetric determination of antibacterial drug gemifloxacin in solubilized systems at multi-walled carbon nanotubes modified glassy carbon electrode

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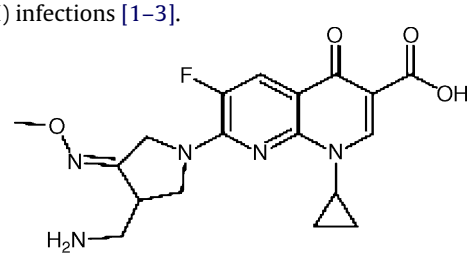
ABSTRACT

A sensitive electroanalytical method for determination of gemifloxacin in pharmaceutical formulation has been investigated on the basis of the enhanced electrochemical response at multi-walled carbon nanotubes modified glassy carbon electrode in the presence of CTAB. Solubilized system of different surfactants including SDS, Tween-20 and CTAB were taken for the study of electrochemical behaviour of gemifloxacin at modified electrode. The reduction peak current increases in the presence of CTAB while other surfactants show opposite effect. The modified electrode exhibits catalytic activity, high sensitivity, stability and is applicable over wide range of concentration for the determination of gemifloxacin. The mechanism of electrochemical reduction of gemifloxacin has been proposed on the basis of CV, SWV, DPV and coulometeric techniques. The proposed squarewave voltammetric method shows linearity over the concentration range 2.47–15.5 μg/mL. The achieved limits of detection (LOD) and quantification (LOQ) are 0.90 ng/mL and 3.0 ng/mL respectively.

1. Introduction

Gemifloxacin (A) is a new enhanced affinity, synthetic flouronapthyridine quinolone antibacterial agent used for the treatment of respiratory problems; acute bacterial exacerbation of chronic bronchitis (AECB), community-acquired Pneumonia (CAP) and urinary tract (UTI) infections [1–3].



(A)

There have been few reported analytical methods for the estimation of gemifloxacin viz., high-performance liquid chromatography–tandem mass spectrometry (LC–MS–MS) [4,5], microchip electrophoresis [6], chiral high-performance liquid chromatography [7] and chiral counter-current chromatography [8].

Survey of literature reveals that there is no comprehensive electrochemical study available concerning the redox behaviour of gemifloxacin. Present communication reports determination of gemifloxacin in pharmaceutical formulation at MWCNTs-GCE in solubilized systems.

Electrode surface modification is a field of paramount importance in the modern electrochemistry especially due to the various application possibilities of modified electrodes. In recent years chemically modified glassy carbon electrodes (CMEs) have received increasing attention due to their potential applications in various analyses and also due to its relative ease of electrode preparation and regeneration [9]. Carbon nanotubes (CNTs) are one of the most important nanomaterials due to their high chemical stability [10], high surface area, high mechanical properties, unique electrical conductivity [11], metallic, structural characteristics [12] and mechanical strength and elasticity [13]. Carbon based electrodes are currently in widespread use in electroanalytical chemistry, because of their broad potential window, low cost, rich surface chemistry, low background current and chemical inertness [14–16].

Surfactants have been widely used in chemistry and in particular affecting several electrochemical processes. Due to the distinct amphiphilic structure and being surface active, surfactants are used in electrochemical investigations [17,18]. Surfactant aggregates such as bilayers, cylinders, or surface micelles adsorbed on electrode surface in solution with surfactant concentration above the critical micelle concentration. It is well documented that the modification of electrode surface by the surfactant increases elec-

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tron transfer rate between the electrode surface and analyte [19,20] and also improves the detection limits.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical reagent grade quality and employed without further purification. Multiwalled carbon nanotube with a 95% purity, o.d. = 10–20 nm, i.d. = 5–10 nm and 0.5–50 μm tube length were obtained from Aldrich. Gemifloxacin (99% pure) was obtained from Aristo Pharmaceutical PVT. Ltd. Tablet containing gemifloxacin (*Gemiquin*) labled 320 mg were obtained from commercial sources. KCl (1.0 mol/L) solution was prepared in double distilled water and used as supporting electrolyte. Stock solutions of gemifloxacin (1.0 mg/mL) were prepared in different electrolytes DMF, CTAB, SDS and Tween 20.

2.2. Analytical procedure

2.2.1. Pharmaceutical preparation

Ten tablets were weighed and the average mass of per tablet was determined. A portion of the finely grounded material equivalent to 320 mg of gemifloxacin accurately weighed and transferred into the 100 mL calibrated flask containing 70 mL of surfactant solution. The content of the flask was sonicated for about 15 min and then made up to the volume with the surfactant solution. An aliquot of the solution was then analyzed according to the proposed voltammetric procedure.

2.2.2. Fabrication of MWCNTs modified glassy carbon electrode

Before each measurement, the GCE was polished on a polishing micro-cloth with 0.5 μM alumina powder and rinsed thoroughly with redistilled water, followed by sonication for 5 min in an ultrasonic bath. The electrode was then transferred to the supporting electrolyte and potential in the range of −0.1 to −1.6 V was applied in a regime of cyclic voltammetry for 20 cycles until a stable voltammogram was achieved. Before the modification of the GCE surface, the MWCNTs were pretreated as reported in literature [21]. The glassy carbon electrode was coated by dropping 10 μL dispersions of MWCNTs solution and processed by vacuum drying.

2.3. Apparatus

Electrochemical measurements were performed using a μ-Autolab type III (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat–galvanostat having 757 VA computrace software. The utilized electrodes are MWCNTs-GCE as working electrode, Ag/AgCl (3.0 mol/L KCl) as reference electrode. The electrochemical cell is a Metrohm 663 VA stand. Controlled potential coulometric experiments were carried out using an Autolab Potentiostat/Galvanostat PGSTAT Metrohm 663 VA stand as electrochemical cell, fitted with a PC provided with the appropriate GPES 4.2 software. All the solutions examined by electrochemical technique were purged for 10 min with purified nitrogen gas, after which a continuous stream of nitrogen was passed over the solutions during the measurements. All pH-metric measurements were made on a Decible DB-1011 digital pH meter fitted with a glass electrode and a saturated calomel electrode as reference, which was previously standardized with buffers of known pH.

3. Results and discussion

3.1. Optimization conditions for determination of gemifloxacin

3.1.1. Effect of pH

The effect of different supporting buffers (B-R, acetate, borate, citrate and phosphate) on the current response of gemifloxcain is studied in order to assess their impact on the monitored electroanalytical signal. The best results with respect to sensitivity accompanied with sharper response were obtained with phosphate buffers. Thus study was made in phosphate buffers of pH range 2.0 to12.0 at a target concentration of 9.6 μg/mL aqueous gemifloxacin solution (Fig. 1A).

The relation between E_p of the wave and pH of the medium over the range 2.0–12.0 may be expressed by the following expressions:

$$\text{SWV}: \quad E_p \ (\text{V}) \ (\text{vs. Ag/AgCl}) = 0.0562 + 1.025 \ \text{pH}; \quad r^2 = 0.996$$
$$\text{DPV}: \quad E_p \ (\text{V}) \ (\text{vs. Ag/AgCl}) = 0.0523 + 1.045 \ \text{pH}; \quad r^2 = 0.991$$

With the rise in pH the peak potential shifted towards more negative potential which indicated the prior protonation of gemifloxacin. The height of the peak reaches maximum at pH 2.0. Therefore, pH 2.0 was chosen as the optimum one for the determination of gemifloxacin.

3.1.2. Effect of CTAB concentration

Cathodic peak current increases steadily in the beginning with increase in concentration of CTAB and reaches a maximum at 1.5×10^{-3} mol/L CTAB and after that deceases continuously (Fig. 1B). It may be interpreted that at 1.5×10^{-3} mol/L CTAB the adsorption behaviour changes from monomer adsorption to monolayer adsorption with increase in concentration of CTAB at the electrode surface. However peak current decrease with further increase in CTAB concentration, it may be due to the inhibition of electron transfer by aggregates of micelles. Another reason for decrease in peak current is the increase of hydrophobicity of CTAB micelles that might decrease the electron transfer rate constant [22] and result in the decrease of peak current at high CTAB concentration.

3.1.3. Effect of MWCNTs amount on the behaviour of modified electrode

The previous studies on the electrochemical behaviour of MWCNTs-GCE also support the observation that the kinetics of the electrode processes and sensitivity of the measurements improves on this electrode [23,24]. Fig. 1C shows that peak current increases with volume of MWCNTs up to 10 μL and then decreases inversely due to large background current. This is related to the thickness of the film. If the film was too thin, the gemifloxacin amount adsorbed was small resulting in the small peak current. When it was too thick, the film conductivity reduced and the film became not as stable as MWCNTs could leave off the electrode surface. Thus it blocks the electrode surface and hence the peak current decreases. So 10 μL MWCNTs is the optimized condition in this study.

3.2. Characterization of the modified electrode

Surface morphological studies of the modified electrode are carried out by scanning electron microscopy (SEM) using Philips SCI quanta 400 instrument. Fig. 2 shows the scanning electron micrograph of MWCNTs-GCE. It can be seen that the MWCNTs were seen in the form of tubes some of which twisted together.

Further the microscopic areas of the MWCNTs-GCE and the bare GCE is obtained by cyclic voltammetry using 1.0 μM $K_4Fe(CN)_6$ as a redox probe at different scan rates. For an irreversible process, the