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Fabrication of carbon-based nanomaterial composite electrochemical sensor for the monitoring of terbutaline in pharmaceutical formulations

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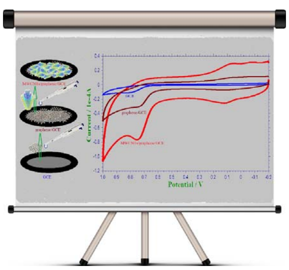
GRAPHICAL ABSTRACT



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ABSTRACT

The present investigation is focused on the development of a chemical sensor made by the modification of glassy carbon electrode (GCE) with graphene followed by multi walled carbon nanotubes (MWCNTs) towards the quantitative monitoring of Terbutaline (TB). The developed sensor was characterized with cyclic voltammetry, scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) studies. The detailed electrochemical redox behavior of TB was examined and possible redox mechanism was proposed. We have studied the effect of pH of phosphate buffer solution (PBS) on the redox behavior of TB and the results suggest that the pH-4.5 was an optimum pH. From the effect of scan rate results, it was concluded that the redox process was controlled by diffusion process and the kinetic parameters were calculated. The effect of concentration of TB was studied and calibration plot was constructed to study the limit of detection and limit of quantification and it was found to be as 6.527×10^{-7} M and 2.175×10^{-6} M respectively. The repeatability, reproducibility and stability of MWCNTs/graphene/GCE, suggest that the developed sensor was superior in condition. The developed sensor was used for the estimation of TB in pharmaceutical formulations and the results were found to be in satisfactory range.

1. Introduction

Terbutaline (TB) is a synthetic β2 – adrenologic agonist, which was widely used for the treatment for asthma and many diseases related to muscle constriction and expansion. This was also used to delay the preterm labor for up to 48 h [1–5]. TB is fast acting bronchodilator which can be used in various methods including oral, subcutaneous, intramuscular or intravenous [6]. TB has wide range of applications in the treatment of many diseases, however due to its carcinogenic effect; the usage of TB drug was warned by the United States − Food drug administration (US – FDA). In some respiratory diseases, the overdose of TB can lead to tremor, tachycardia, cephalalgia, gastrointestinal disturbances and sometimes fatal significances. Since the higher concentrations of TB in human body may cause abnormal behavior in humans, the usage of TB by athletes was prohibited in Olympic games and currently this was in the prohibited list of world anti-doping agency

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(WADA) [7–10]. Based on this description, there is a considerable interest for the qualitative and quantitative determination of TB in the pharmaceutical formulations. Currently, many analytical methods are existing for the monitoring of TB, which includes chromatography, spectrophotometry, high performance liquid chromatography (HPLC) and other techniques [11–17]. However, the above mentioned methods require complicated procedures and sophisticated instrumentation. Nevertheless, based on the simplicity in handling the instrument, rapidness and ease in analyzing the results, sensitivity and portable nature, the electroanalytical techniques have received considerable interest for the qualitative and quantitative analysis of various drugs, pesticides, environmental pollutants, food and biologically important molecules [18–23].

Electroanalytical techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and Tafel plot experiments were based on the principle of applying the potential to the analyte, that undergo either oxidation or reduction and causes electron transfer in the cell. The electron transfer in the cell produces current flow, and the amount of current flow is measured through the voltammetry method. The voltammetric methods typically have a three electrode system with the combination of reference electrode, counter electrode and working electrode in which working electrode plays a critical role in measuring the current flow in the cell. However, the conventional working electrodes like carbon paste electrode, glassy carbon electrode, platinum electrode etc., has surface fouling nature that leads to the poor sensitivity. To overcome this problem and to get a better sensitivity the conventional working electrode surfaces were modified with different conducting and catalytic materials, nanoparticles, clays and enzymes [24].

Nowadays nanomaterials have received global concern because of its unique size, shape and special characteristics. Recently carbon and carbon based nanomaterials like fullerenes, MWCNTs and graphene have emerged as very promising utensils for the development of semi conducting devices [25]. Based on the structure of carbon based nano materials, carbon allotropes were classified as 0D (carbon quantum dots), 1D (nanotubes), 2D (carbon flakes and graphene oxides), and 3D (carbon aerogels) materials [26]. Especially after the discovery of MWCNTs by Iijima in 1991 they have played very much important role in almost all areas of science [27]. Due to its large surface area, good conductivity and catalytic nature, these materials were successfully used for the fabrication of electrochemical sensors and biosensors [19,28–30]. Graphene and MWCNTs facilitates large surface area over the bare electrode surface and due its conductive nature, it facilitates fast electron transfer rate for the redox behavior of an analyte. Based on the above important descriptions of MWCNTs and graphene, we have developed an electrochemical sensor with the graphene and MWCNTs towards the determination of TB.

The present work explores on the development of an electrochemical sensor for the sensitive monitoring of TB based on the modification of GCE with graphene suspension and followed by MWCNTs. This report also consists of the characterization of the sensor and optimization of the supporting electrolyte pH. The detailed electrochemical redox response of TB was investigated and the possible electrochemical redox mechanism was successfully exhibited. The kinetic parameters such as charge transfer coefficient, heterogeneous rate constant and analytical parameters including limit of detection and limit of quantification values were deduced. The repeatability, reproducibility and stability of the developed sensor were demonstrated. The fabricated electrochemical sensor greatly broadens the sensing application of TB and it can be utilized to detect the TB in various cough syrups, injections and tablets. Further the proposed method reduces the time consumption and improves the sensitivity and specificity.

2. Materials and methods

2.1. Materials

All materials were received from commercial source and used without any further purification. Terbutaline (TB) was from Sigma-Aldrich and Multi walled carbon nanotubes (MWCNT) were from Dropsens, Edificio CEEI, Llanera (SPAIN). Graphene was from Acros Organics, $K_4[Fe(CN)_6]$ and Na_2HPO_4 were from Merck specialties Pvt. Ltd, Mumbai and $K_3[Fe(CN)_6]$, NaH_2PO_4 were received from Fisher Scientific India Pvt. Ltd.

2.2. Methods

The electroanalytical techniques which were used in the present analysis namely cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy were accomplished by using CH Instruments model CHI 660D, Texas, Austin with the aid of conventional three electrode system having saturated calomel electrode as a reference electrode (provided by CH Instruments (CHI150)), platinum wire (provided by CH Instruments (CHI115)) as a counter electrode and MWCNTs/graphene/GCE (GCE was received from CH Instruments (CHI104)) as a working electrode. The surface morphology was studied by using the scanning electron microscopic (SEM) analysis using Carl Zeiss AG (Supra 55VP) with an acceleration voltage of 5e30 kV. The Phosphate buffer solutions (PBS) were made to anticipated pH values by using ELICO pH meter and glass electrode. The homogeneous suspension of MWCNTs was prepared by using Toshibha ultra sonication bath made in India, all the measurements were carried out in Department of Chemistry, Sri Venkateswara University, Tirupati, Andhra Pradesh, India.

2.3. Preparation of MWCNT/graphene/GCE sensor

Erstwhile to the modification of GCE, we have polished the GCE surface with alumina slurry having different sizes of 1 μm, 0.3 μm and 0.05 μm for getting mirror like shine. After receiving mirror like shine 5 μL of graphene suspension in ethanol (1 mg/1 mL) solution was drop casted on to the surface of GCE and dried for half an hour. The graphene suspension was physically adsorbed onto the surface of GCE and was denoted as graphene/GCE. The graphene/GCE was further modified with MWCNTs suspension in ethanol. A 5 μL of MWCNTs suspension in ethanol (1 mg/1 mL) was drop casted on to the surface of graphene/GCE and dried. The obtained electrode was here after referred to as MWCNTs/graphene/GCE.

3. Results and discussions

3.1. Characterization of electrodes

We have characterized the developed electrodes GCE, graphene/GCE, MWCNTs/GCE, graphene/MWCNTs/GCE and MWCNTs/graphene/GCE with the aid of CV technique and the CV responses were observed for 1 mM $[Fe(CN)_6]^{-3}$ in 0.1 M KCl at different electrodes. From Fig. 1a, we have observed the CV response of $[Fe(CN)_6]^{-3}$ at bare GCE, where a reversible redox couple for $[Fe(CN)_6]^{-3}$ with a peak to peak separation of (ΔE_p) 92 mV and peak to peak current ratio of (i_p^a/i_p^c) 0.989 was observed. The modification of GCE with graphene led to the increase in the current response to -2.026×10^{-5} A with a peak to peak separation of (ΔE_p) 107 mV and peak to peak current ratio of (i_p^a/i_p^c) 0.97, suggesting that the immobilized graphene facilitates the conductive nature. Further, the modification of graphene/GCE with MWCNTs led to the further increase in the current response from -2.026×10^{-5} A to -2.571×10^{-5} A with a peak to peak separation of (ΔE_p) 82 mV and peak to peak current ratio of (i_p^a/i_p^c) 1.036 confirming the conductive nature of MWCNTs on the surface of graphene/