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Sensitive detection of sulfasalazine at screen printed carbon electrode modified with functionalized multiwalled carbon nanotubes

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ABSTRACT

A new home-made screen-printed carbon electrode (SPCE) modified with a functionalized multiwalled carbon nanotubes (MWCNTCOOH) and benzyl acetate (BA) was prepared for electrochemical determination of sulfasalazine (SSZ). Determination of SSZ was carried out by differential pulse voltammetry (DPV) in 0.04 mol L^{-1} Britton-Robinson buffer solution of pH 1.7 at −40 mV (versus Ag/AgCl) at MWCNTCOOH/BA-SPCE. The electrochemical behavior of the modified SPCEs was investigated by cyclic voltammetry and impedance spectroscopy. The effects of various parameters on the response of the electrode such as type of modifier, pH of the buffer, and DPV parameters were investigated. The reduction peak current obtained from DPV of SSZ increased linearly with its concentration at the ranges of 1.0–14 μmol L^{-1} and 14–70 μmol L^{-1} with sensitivities of 1.84 and 0.48 μA μM^{-1} cm^{-2}. The relative standard deviation (RSD%) of seven replicates of current measurements for a 20 μmol L^{-1} of SSZ solution was 3.2%. The detection limit of the method was found to be 0.3 μmol L^{-1}. The prepared sensor was successfully applied for the determination of SSZ in pharmaceutical formulation and biological fluid samples.

1. Introduction

Sulfasalazine (SSZ) is a sulfonamide that belongs to the important class of medications called anti-inflammatories. It is commonly used in the treatment of inflammatory bowel disease such as ulcerative colitis and Crohn's disease and reduces the symptoms and slow-down the progress of rheumatoid arthritis [1,2]. It is employed in clinical practice as 5-aminosalicylic acid (5-ASA; mesalazine) precursor. When the drug is given orally, it is partly absorbed unchanged and partly cleaved to 5-ASA and sulfapyridine (SP) by bacterial azo reductase in the large intestine [3]. The active part, 5-ASA, is produced in the colon by bacterial reduction of azo-bridge. Also, the antitumor and antimicrobial activities of the SSZ and their alkaline metal (II) complexes have been evaluated [4].

Numerous analytical methodologies for clinical monitoring and pharmacologic studies of SSZ and its metabolites in different biological matrices have been reported including liquid chromatography [5,6], high performance liquid chromatography (HPLC) [7–9], spectrophotometry [10], luminescence [11], enzyme-linked immunosorbent assay [12] and capillary electrophoresis mass spectrometry [13]. Some of these methods offer good detection limits and wide working concentration ranges. However, expensive instrumentation, complicated pretreatment procedures in some cases and running costs caused large efforts focus on the development of simple and effective analytical methods for the determination of SSZ. Nowadays, electroanalytical techniques comprise promising methods for the determination of pharmaceutical compounds in different matrices have been increased because of their high sensitivity, specific response, simplicity, low cost, and relatively short analysis time [14]. Among these techniques, voltammetry has been proved useful to determine sulfonamide drugs such as SZZ. Different electrodes were used in voltammetric determination of SSZ including molecularly imprinted polymer modified carbon paste electrode [15], antimony film electrode [16], bismuth film electrode [17], mercury electrode [18] and glassy carbon electrode [19]. Screen printed carbon electrodes (SPCEs) are disposable electrodes and has ability to be miniaturized to reduce consumption of sample and potential portability that are great promise for determination of drugs and biological samples [20–23]. Multiwalled carbon nanotubes (MWCNTs) are porous carbon materials possessing properties such as high chemical and mechanical stability, high surface area, and unique electrical conductivity [24,25]. Combination of screen-printed electrodes and carbon nanotubes improves electronic transfer properties of the resulting electrodes in high sensitivity and low detection limits and decreases overpotentials [26–30]. These properties provide an excellent platform for modification of SPCEs with MWCNTs.

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The present work, therefore, aims to apply MWCNTs modified screen-printed carbon electrode as a working electrode for measurement of SSZ by differential pulse voltammetry method. The resulting electrode exhibited high sensitive response toward SSZ with low detection limits. The proposed method showed adequate simplicity, sensitivity, and effectiveness in determination of SSZ in biological samples. To the author's knowledge, there is no previous report on the electrochemical detection of SSZ using functionalized MWCNTs modified screen printed carbon electrode.

2. Experimental

2.1. Apparatus

A Metrohm model 746 VA Trace Analyzer processor and 747 VA stand (Herisau, Switzerland) equipped with Ag/AgCl/3 mol L^{-1} KCl reference electrode and a platinum counter electrode was employed. The modified SPCEs were used as the indicator electrodes for electrochemical measurements. Electrochemical impedance spectroscopy (EIS) studies were carried out using an Autolab 302N potentiostat/galvanostat/frequency-response analyzer PGST302N, controlled by GPES/FRA2 Version 4.9 (Metrohm, Utrecht, Netherlands). Impedance analysis of the prepared SPE modified electrodes were performed in 1 m mol L^{-1} of $[Fe(CN)_6]^{3-/4-}$(1:1) mixture with KCl 0.1 mol L^{-1} as a redox probe. The impedance spectra were recorded in the frequency range of 0.1–100 kHZ with an applied sinusoidal wave potential of 25 mV. The Nyquist (imaginary impedance versus real impedance) plots were also recorded. The pH measurements were carried out using a Corning 125 pH meter (LabEquip Ltd., Ontario, Canada) equipped with a combined glass electrode. Ultrasonic agitating of inks was performed to disperse of particles in solvent by a Branson cleaner model 1510R MTH sonicator (Emerson Electric Co. Danburg, USA). Deionized water was obtained from an AquaMax system (Young-Lin corp., Korea).

2.2. Reagents

Sulfasalazine (SSZ) was kindly supplied by Mehr Pharmacy Company, Tehran, Iran and was used as received. All chemicals used were of the analytical grade and purchased from Merck (Darmstadt, Germany). Graphite powder (size ⩽50 mm) was purchased from Fluka. Multiwalled carbon nanotubes (MWCNTs) with purity >95% with an external diameter between 10 and 20 nm were provided by the US Research Nanomaterials Inc. (Houston, USA). A stock solution of 1.0×10^{-3} mol L^{-1} SSZ was prepared in water and used to prepare the other concentrations by dilution with Britton–Robinson (BR) buffer as supporting electrolyte. BR buffer was prepared by mixing of solutions 0.04 mol L^{-1} acetic, phosphoric and boric acids and adjusted to the desired pH with additions of 0.2 mol L^{-1} sodium hydroxide solution. All solutions were freshly prepared using deionized double distilled water.

2.3. Functionalization of MWCNT

MWCNTs were modified by acid group via oxidation process using concentrated acid solution. In brief, 75 mg amount of MWCNTs was dispersed in 10 mL of 3:1 concentrated H_2SO_4 and HNO_3 in a water bath for 8 h at 50 °C with the aid of ultrasonic agitation. After cooling the suspension to room temperature, it was diluted with 50 mL deionized water and then vacuum filtered through a 0.2 μm polycarbonate membrane. The solid was rinsed thoroughly with deionized water until the filtrate reaches to neutral pH and finally dried under vacuum for 24 h at 40 °C. The prepared sample is carboxylic acid-functionalized MWCNT (MWCNTCOOH) [33].

2.4. Fabrication of screen printed carbon electrodes (SPCEs)

2.4.1. Bare electrodes

The bare screen-printed carbon electrodes (SPCEs) were constructed home-made as described previously [31,32]. First, the connector of the electrodes (5×35 mm; 0.5 mm thick) were printed onto the PVC substrate by home-made silver ink which was prepared by mixing 98% Ag powder and 2% PVC in mixture 1:1 of acetone–cyclohexanone. Afterwards, the surface of reaction region of working electrodes were printed over silver connector pad by dispersing of 93% (w/w) graphite powder and 7% (w/w) PVC in 1:1 (v/v) mixture of acetone–cyclohexanone. Finally, the insulator layer was printed on the SPCEs to achieve a round shape of the working electrode with a conductive track radius of 3.5 mm. After deposition of each layer, a drying process was performed by keeping the PVC substrate at room temperature for 3 h. Two kinds of modified bare SPCE were fabricated with the same procedure except for using carbon ink formulation as 59% (w/w) graphite powder, 35% (w/w) ionic liquid [OMIM][PF_6] (IL) or benzyl acetate (BA) and 6% (w/w) PVC binder. The prepared electrodes were denoted as IL-SPCE and BA-SPCE, respectively. The electrodes were stored in dry place at 4 °C in refrigerator before use.

2.4.2. Preparation of MWCNTCOOH/BA-SPCE

Prior to modification of the electrode surface, the surfaces of BA-SPCEs were activated by sweep potential from 1000 to −1000 mV twenty times with a scan rate of 50 mV s^{-1} in 0.1 M HCl/KCl solution. Afterwards, the surface of the SPCE working electrode was modified with MWCNTCOOH. A suspension containing 5 mg functionalized MWCNTCOOH in 5 mL of DMF: water (1:1) solvent was prepared and sonicated for 4 h to achieve a homogeneous and stable black dispersion solution. For a typical fabrication of MWCNTCOOH/BA-SPCE, 7 μL of the MWCNT suspension was drop casted onto the bare working electrode surface followed by a drying process at room temperature for 8 h. After drying MWCNTCOOH/BA-SPCEs in air, it was rinsed with deionized water three times to remove the impurities and cleaning working electrode surface. For comparison, the BA-SPCE modified with non-functionalized MWCNT (MWCNT/BA-SPCE) was prepared according to the same procedure.

2.5. Procedure for voltammetric analysis

A 15 mL aliquot of the BR buffer (0.04 mol L^{-1}; pH 1.7) as a supporting electrolyte was placed in the dry and clean voltammetric cell. The MWCNTCOOH/BA-SPCE was immersed in buffer solution. After purging the solution with highly pure nitrogen gas for 10 min, differential pulse voltammetry (DPV) was then performed from 150 to −350 mV (versus Ag/AgCl electrode) at a scan rate of 60 mV s^{-1} employing pulse amplitude of −80 mV with 50 mV pulse width. After recording the blank voltammogram, an appropriate aliquot of the SSZ stock solution was introduced to the voltammetric cell to achieve a suitable concentration of the drug and the voltammogram was again recorded for the same electrode. Quantification of SSZ was performed by determination of the reduction peak current at −40 mV. The average peak heights were used for construction of the calibration curve. Each experiment was triplicate at the same conditions.

2.6. Analysis of real samples

Contents of ten SSZ tablets (Mehr Pharmaceutical Company, Tehran, Iran) equivalent to 500 mg per tablet were completely homogenized and fine powdered. An adequate portion of the powder was accurately weighted and sonicated in water containing two drops of 2 mol L^{-1} NaOH solution for 10 min. Then, the