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Determination of gemfibrozil in pharmaceutical and urine samples by square-wave adsorptive stripping voltammetry using a glassy carbon electrode modified with multi-walled carbon nanotubes within a dihexadecyl hydrogen phosphate film

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ABSTRACT

Glassy carbon electrode modified with functionalized multi-walled carbon nanotubes within a dihexadecyl hydrogen phosphate film was used to develop a sensitive and simple square-wave adsorptive stripping voltammetric (SWAdSV) method for the determination of gemfibrozil. The cyclic voltammograms obtained showed one irreversible anodic peak for gemfibrozil at a potential of 1.3 V using a 0.1 mol L^{-1} phosphate buffer solution (pH 2.0). The cyclic voltammetric responses were studied with regard to scan rate, and the number of electrons transferred during the oxidation process was calculated. A calibration curve for gemfibrozil in the concentration range from 75 to 1000 nmol L^{-1} with a detection limit of 53 nmol L^{-1} were obtained. The proposed SWAdSV method was successfully applied to determine gemfibrozil in pharmaceutical and urine samples with good accuracy and precision.

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1. Introduction

Gemfibrozil (GEM) 5-(2,5-dimethylphenoxy)-2, 2-dimethylpentanoic acid (Fig. 1), is a highly effective agent that is used for the treatment of hyperlipidemia, which is a growing disease of medical concern. GEM, a fibric acid derivative, reduces the levels of triglycerides, cholesterol, and low-density lipoprotein (LDL) in the blood and increases the concentrations of cholesterol carried in high-density lipoprotein (HDL); these changes are associated with a reduced incidence of coronary heart disease [1,2]. More than 90% of orally administered GEM is absorbed, and most of the absorbed drug is excreted in the urine [3]. Its plasma half-life is about 1.5 h, and the peak blood levels of about 20 μg mL^{-1} are reached 1–2 h after the ingestion of a single 600-mg dose. Thus, the determination of GEM in pharmaceutical formulations and urine is necessary for quality-control procedures in the industry, in order to ensure the correct dose in patients during treatment and for physiological pharmacokinetics.

A review in the literature reveals that several methods have been developed for the determination of gemfibrozil: high-performance liquid chromatography (HPLC) [4–8], gas chromatography (GC) [9–11], spectrofluorimetry [3,12], polarography [13], and potentiometry [14]. Nevertheless, most of these methods just cited require relatively expensive instrumentations, a long time of analysis, and/or an analyst with dedicated skills. Notwithstanding, as far as we know, no procedure has ever been reported for the determination of GEM in pharmaceutical formulation and urine using a voltammetric method and a glassy carbon electrode modified with carbon nanotubes.

Carbon nanotubes (CNTs) have attracted increasing attention due to their special structure and unique mechanical, electronic, and electrochemical properties. CNTs used as electrode material enable fast electron-transfer reactions that can improve the electrocatalytic properties [15–22]. Although CNTs have so many merits, they are insoluble in most solvents, which can limit their application. Moreover, an aqueous suspension of as-prepared CNTs is usually unstable, due to its hydrophobic surface [23]. The functionalization of CNTs is used to increase the CNTs solubility. A chemical oxidation method is commonly used. In this method, a mixture of sulfuric and nitric acids is used for eliminated metallic impurities, and it enhances the dispersibility of the CNTs in aqueous solution by the formation of carboxyl and hydroxyl groups

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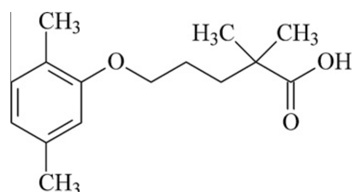

Fig. 1. GEM molecular structure.

either at the ends or at the sidewall defects of the nanotubes structure.

Dihexadecyl hydrogen phosphate (DHP) is a hydrophobic surfactant that has two long hydrocarbon chains linked to the phosphate group which self-assembles into multiple bilayer structures that are similar to lipid bilayers; this behavior allows the dispersal of CNTs as well as the preparation of an aqueous stable and homogeneous suspension [24–29].

In this study, a multi-walled carbon nanotube and a DHP (MWCNTs-DHP) film-modified glassy carbon electrode were prepared and employed for the development of a convenient and sensitive square-wave adsorptive stripping voltammetric (SWAdSV) method to determine GEM in pharmaceutical and urine samples.

2. Experimental

2.1. Reagents

Stock solution (1.0×10^{-3} mol L^{-1}) of gemfibrozil (Sigma–Aldrich) was freshly prepared in ethanol (Sigma–Aldrich). Dihexadecyl hydrogen phosphate and multi-walled carbon nanotubes (20–30 nm in diameter and 0.5–2.0 μm in length; purity: ⩾95%) were obtained from Sigma–Aldrich. Other reagents used were of analytical grade, and all solutions were prepared using ultra-purified water (resistivity greater than 18 MΩ cm) supplied by a Milli-Q system (Millipore®).

2.2. Apparatus

All voltammetric experiments were performed using an AUTOLAB PGSTAT-30 (Ecochemie) potentiostat/galvanostat controlled with the GPES 4.0 software. A three-electrode cell system was used, with a platinum wire as auxiliary electrode, an Ag/AgCl (3.0 mol L^{-1} KCl) as reference electrode, and a glassy-carbon electrode (GCE) (4 mm in diameter) or a dihexadecyl hydrogen phosphate-modified glassy-carbon electrode (DHP/GCE) or a dihexadecyl hydrogen phosphate/multi-walled carbon nanotube-modified glassy-carbon electrode (MWCNTs-DHP/GCE) as working electrode.

The GEM determination using HPLC was carried out using an LC-10AT Shimadzu system with a UV/Vis detector (SPD-M10-AVP) set at a wavelength of 232 nm and a Shim-Pack CLC-ODS (4.6×150 mm, 5 μm) chromatographic column. The mobile phase was an acetonitrile/water solution (70:30, v/v) adjusted to pH 2.5 with 85% phosphoric acid. The flow rate was 1.2 mL min^{-1}, and the injection volume was 50 μL [6].

2.3. Preparation of the MWCNTs-DHP-modified electrode

Initially, the GCE was polished to mirror finish using an ultra-fine sand paper and 1.0 μm and 0.5 μm of alumina slurry. After being rinsed with ultrapure water, the polished GCE was sonicated for 5 min in ultrapure water and dried at room temperature.

Carbon nanotubes were purified to remove metallic impurities with 2.0 mol L^{-1} HCl solution and ultrapure water; this was followed by treatment with a mixture of HNO_3/H_2SO_4 solution (3:1, v/v), both concentrated, for 12 h at room temperature to allow the introduction of polar hydrophilic surface groups, mainly the carboxyl group at the ends or at the sidewall defects of the nanotube structure. After this, the suspension was centrifuged, and the solid was washed several times with ultrapure water until pH 6.5–7.0 was reached, and then dried at 120 °C for 6 h [30,31].

The MWCNTs-DHP suspension was prepared by dispersing 1 mg of functionalized MWCNTs and 1 mg DHP into 1 mL of ultrapure water that was placed in an ultrasonic bath for 120 min.

The MWCNTs-DHP/GCE was made by dropping 15 μL of MWCNTs-DHP suspension on the polished surface of the glassy carbon electrode using a micropipette and leaving it to dry at room temperature for 12 h in air. Due to the evaporating solvent, a uniform and stable MWCNTs-DHP film was obtained on the electrode surface.

2.4. Analytical procedure

The MWCNTs-DHP/GCE was first stabilized in 10 mL of 0.1 mol L^{-1} phosphate buffer solution (pH 2.0) by 50 cyclic voltammetric sweeps between −0.2 and 1.4 V. Then, the electrode was transferred into another glass conventional cell containing 10 mL of 0.1 mol L^{-1} phosphate buffer solution (pH 2.0), and aliquots of the stock solution of GEM were added.

The GEM determinations in pharmaceutical and urine samples were carried out by square-wave adsorptive stripping voltammetry. A systematic study of SWV parameters was conducted, and the best chemical conditions were initially evaluated. After optimization of the parameters, the SWAdS voltammograms were obtained in a potential range from 1.10 to 1.45 V vs. Ag/AgCl (3.0 mol L^{-1} KCl) with an accumulation time of 300 s, a square-wave frequency of 40 Hz, a pulse amplitude of 45 mV, and a scan increment of 3 mV. The analytical curve was constructed using the SWAdS voltammograms obtained after the successive addition of aliquots of the GEM stock solution into the electrochemical cell containing 10 mL of 0.1 mol L^{-1} phosphate buffer solution (pH 2.0). Each concentration was a measurement in triplicate. The artificial urine and pharmaceutical samples were analyzed in triplicate using the standard addition method.

2.5. Sample preparation

Commercial samples (600 and 900 mg GEM/tablet) were obtained from a local market. Artificial urine was prepared as described elsewhere [32]. The urine samples were spiked with adequate amounts of GEM stock solution to obtain concentration of 1.0×10^{-5} mol L^{-1}.

Ten GEM tablets were weighed and ground to a homogeneous powder in a mortar. A certain amount of drug was accurately weighed, transferred into a 50-mL calibrated flask, and completed to the volume with ethanol to prepare a solution equivalent to a GEM stock solution. The sample contained in the flask was sonicated for 30 min to complete dissolution. After an appropriate aliquot was diluted with supporting electrolyte, an aliquot of 250 μL was transferred to the voltammetric cell.

Considering the range of the calibration curve (analytical curve), aliquots of 250 μL and 800 μL of artificial urine that were spiked were placed in a conventional glass cell containing 10 mL of supporting electrolyte.

3. Results and discussion

3.1. Electrocatalytic oxidation of gemfibrozil on the MWCNTs-DHP/GCE

The electrochemical behavior of GEM was studied by cyclic voltammetry in a 0.1 mol L^{-1} phosphate buffer solution (pH 2.0). The

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