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Development of a new electrochemical sensor for verapamil based on multi-walled carbon nanotube immobilized on glassy carbon electrode

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ABSTRACT

A sensitive and selective method is presented for the voltammetric determination of verapamil using a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNTs/GCE). The oxidation peak current of verapamil at 1.02 V (vs. Ag/AgCl) is remarkably increased on the MWCNTs/GCE. Scanning electron microscopy (SEM) was used for characterization of the modified electrode surface. The electrochemical oxidation of verapamil using the MWCNTs/GCE was investigated by cyclic voltammetry. The experimental parameters including chemical and instrumental variables were investigated and optimized for verapamil determination. Under the optimum conditions voltammetric peak currents showed a linear response for verapamil concentration in the range of 2.5–70.0 μM, for both CV and DPV with detection limits of 2.0 μM and 1.6 μM, respectively. The relative standard deviation of five replicates determinations of 15.0 μM verapamil was 3.92%. The interference effects of frequently encountered excipients, additives and common species on the determination of verapamil were also studied. The sensor was successfully applied for verapamil determination in pharmaceutical and spiked human serum samples.

1. Introduction

Verapamil is L-type calcium channel blocker of the phenylalkylamine class [1]. It has been used in the treatment of hypertension, angina pectoris, cardiac arrhythmia, and most recently, cluster headaches [2]. It is also an effective preventive medication for migraine. Verapamil has also been used as a vasodilator, during cryopreservation of blood vessels. Because of all these properties its determination is of interest in analytical chemistry. Several reports using different analytical methods such as high performance liquid chromatography [3–15], gas chromatography [16–18], solid phase micro-extraction [19], FIA [20] and spectrophotometry [21,22] have been published about the determination of verapamil in plasma, urine, drugs and clinical samples. In spite of higher selectivity offered by aforementioned techniques, they are expensive and also suffer from some disadvantages such as complicated and long operational procedure, and high reagent consumption. Among different analytical methods, electrochemical determination has proved to be highly sensitive and reliable with less interference from non-electroactive substances for determination of numerous electroactive components. Some electrochemical techniques have been reported for determination of verapamil including voltammetric determination of verapamil in urine and pharmaceuticals at the surface of the mercury drop [23], bare glassy carbon [24] and gold nanoelectrode [25]. These methods exhibit acceptable sensitivity, but have some disadvantages such as using toxic mercury electrode [23] and complexity due to pre-oxidation of verapamil

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with strong oxidizing agents prior to its electrochemical determination [25].

The electrode surface and its nature, have crucial importance in both selectivity and sensitivity of electroanalytical methods. Bare electrodes have been widely used for determination of different analytes by different electrochemical techniques. In most cases, the bare surfaces do not fulfill the needs required. So, the electrode modification seems to be inevitable. Surveying the literature revealed that a few modified electrodes such as graphite–polyurethane composite electrode [26], glassy carbon electrode modified with a thin film of poly(allylamine hydrochloride) carbon nanotube [27] and Nafion-modified glassy carbon electrode [28] have been used for direct or indirect electrochemical determination of verapamil. It was established that the modification of electrode substrates with multi-walled carbon nanotubes (MWCNTs) causes considerable improvement in detection limit and sensitivity of electroanalytical methods in determination of different biological and pharmaceutical species [29–32]. Thus the construction and application of modified electrodes for the sensitive and selective determination of verapamil in the biological and pharmaceutical samples is of great interest. This paper reports the construction and application of MWCNTs modified glassy carbon electrode (MWCNTs/GCE) in the voltammetric determination of verapamil. The goal of this work was the development of new voltammetric sensor based on the MWCNTs/GCE for the simple and direct determination of verapamil in pharmaceutical and spiked human serum samples without any time-consuming pretreatment steps prior to drug assay. This paper also reports the electrochemical behavior of verapamil on the surface of modified electrode.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed using Ivium potentiostats/galvanostats (CompactStat, Netherland). The three-electrode system consisted of a platinum wire counter electrode, an Ag/AgCl reference electrode, and the multi-walled carbon nanotubes modified glassy carbon electrode (MWCNTs/GCE) as working electrode. An aqueous slurry of alumina powder on a damp smooth polishing cloth was used for manually polishing of GCE (Azar electrode, $d = 2.0$ mm). Ultrasonic (BANDELIN electronic, Germany) was used for cleaning the electrode surface and the suspension agitation in the preparation of the modifier. The pH measurements and adjustments were carried out using a Metrohm744 pH-meter equipped with a combined glass electrode. All measurements were realized at room temperature. Scanning electron microscopy (SEM) was performed with a Hitachi S-4160 (Japan) microscope.

2.2. Reagents

MWCNTs with outer diameter of 8 nm, purity of 95% and length of 10–30 μm were purchased from Neutrino Co., Iran. Verapamil hydrochloride was purchased from Kharazmi Pharmaceutical Company, whose source was Dipharma, Italy. Pharmaceutical form verapamil tablets were supplied from local pharmacies. N,N-dimethylformamide (DMF) and alumina powder (Al_2O_3) were purchased from Aldrich, phosphoric acid (H_3PO_4), sodium phosphate monobasic monohydrate ($NaH_2PO_4{\cdot}H_2O$) and sodium phosphate dibasic dihydrate ($Na_2HPO_4{\cdot}2H_2O$) used for the preparation of phosphate buffer solutions (PBS) were obtained from Merck. Other chemicals and reagents were of analytical reagent grade (from Merck or Riedel-de Haën) and were used without purification. Doubly distilled water was used to wash the glassware, and to prepare all solutions. A stock solution of verapamil (5.0 mM) was prepared by direct dissolution in ethanol and the diluted solutions were prepared daily by accurate dilution with double distilled water. Phosphate buffer solution (pH 5.0) was prepared by mixing the appropriate volume of NaH_2PO_4 (0.15 M) and Na_2HPO_4 (0.15 M) solutions and adjusting the pH to 5.0 using a pH-meter.

2.3. Preparation of MWNTs/GCE

Glassy carbon electrode (GCE) surface was cleaned mechanically by polishing with alumina in water slurry on micro-cloth pad. Adherent Al_2O_3 particles were removed from the electrode surface by rinsing with double distilled water. It was then sonicated in diluted nitric acid solution and further rinsed with distilled water and dried the GCE surface in an oven (80 °C). 1.0 mg of MWCNTs was dispersed in 10.0 mL DMF and sonicated in an ultrasonic for 30 min to obtain a stable suspension. The MWCNTs/GCE was prepared by coating of 10.0 μL MWCNTs suspension on the GCE surface using a micropipette and left to dry under the IR lamp. The MWCNTs/GCE was activated by 50 successive cyclic voltammograms in the potential range of 0–1.2 V (vs. Ag/AgCl) in PBS (pH 5.0) as supporting electrolyte until stable voltammograms were obtained (Fig. S1 in the Supporting Information). The electroactive areas of the MWCNTs/GCE and the bare GC electrodes were measured by CV using 1.0 mM $K_4Fe(CN)_6$ solution containing 0.1 M KCl. The obtained modified GCE (MWCNTs/GCE) was further characterized by SEM.

2.4. Pharmaceutical sample preparation

Three tablets of verapamil containing 40 mg verapamil per tablet (Rouz Darou Pharmacy Co., Iran) were accurately weighed and finely powdered by pestle in a mortar. A quarter weight portion of this powder was first dissolved in an appropriate amount of ethanol with the aid of sonication in order to complete dissolution. Then it was transferred into 250 mL volumetric flask and completed to the volume with distilled water. An aliquot of this solution was then analyzed according to the proposed analytical procedure using calibration curve.

2.5. Serum sample preparation

Drug-free human blood, obtained from healthy helpers, was centrifuged at 4000 rpm for 30 min at room