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Voltammetric determination of 6-mercaptopurine using a multiwall carbon nanotubes paste electrode in the presence of isoprenaline as a mediator

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ABSTRACT

In this study, we describe the application of multiwall carbon nanotubes paste electrode (MWCNTPE) in the presence of isoprenaline (ISPT) as the suitable mediator for voltammetric determination of 6-mercaptopurine (6-MP) in aqueous buffer solution (pH 4.0). The results indicate that the electrode is efficient in terms of its electrocatalytic activity for the oxidation of 6-MP in the presence of ISPT as a mediator. Using chronoamperometry, the catalytic reaction rate constant was calculated at 1.68×10^{-3} μM^{-1} s^{-1}. The catalytic peak current was linearly dependent on 6-mercaptopurine concentration in the range of 0.5–900 μM 6-MP. The detection limit (3σ) obtained by linear sweep voltammetry (LSV) was 0.1 μM. Finally, the proposed method was also examined as a selective, simple and precise electrochemical sensor for the determination of 6-MP in real samples such as urine and tablet.

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1. Introduction

Carbon nanotubes (CNTs) have emerged as a novel class of nanomaterials and consequently, receive considerable interest in a plethora of areas [1–4], none more so than in electrochemistry and electrocatalysis where their use has escalated over the last decade owing to the reported “electrocatalytic” properties of carbon-nanotube-modified electrodes. That is, electrodes were usually made of carbon with a film of nanotubes [5–9]. These properties include reductions in over potentials, increments in the voltammetric peak heights which facilitates lower detection limits and enhanced sensitivities in analytical sensing coupled with little or no observed surface fouling [5–7].

Optimization of CNTs in electrode matrix is one way of obtaining the best condition in preparation of the modified electrodes [10–12]. Olivé-Monllau et al. describe the importance of optimization carbon nanotube ratio in composite materials in preparation of voltammetric sensors [13]. This point is a very important strategy in obtaining best sensitivity and selectivity condition in preparation of modified electrode with carbon nanotubes as a sensor. Addition of carbon nanotubes to electrode matrix can be increased active surface area and kinetic parameter such as electron transfer coefficient (α) and heterogeneous rate constant (k_h) [14–20].

Mercaptopurine is an immunosuppressive drug. It is a thiopurine [21] and used to treat leukemia. This drug is traditionally not recommended during pregnancy but this issue has been debated, and current evidence indicates that pregnant women on the drug show no increase in fetal abnormalities. However, women receiving mercaptopurine during the first trimester of pregnancy have an increased incidence of abortion. Therefore, the drug has the potential to be cancer-causing in humans. Various methods, including high-performance liquid chromatography (HPLC) [22,23], capillary electrophoresis [24–26], electrochemical methods [27–29], fluorescence [30], and spectrophotometric methods [31] have been used for the detection of 6-MP in plasma and urine. However, there still remains certain limitations in spectrofluorometric and chromatographic methods that include selecting a suitable column or mobile phase, finding a suitable reactant for the post-column reaction (in order to increase sensitivity) in liquid chromatography, and facing many interfering substances in spectrofluorometric methods. Most of the methods were reported to suffer from disadvantages such as complicated procedure, long response time, a requirement of expensive instruments, and low detection capability. On other hand, electroanalytical methods have attracted more attention in recent years for environmental and biological compounds determination due to their sensitivity, accuracy, lower cost, and simplicity [32–63].

In the present work, we described initially the preparation of multiwall carbon nanotubes paste electrode in the presence of ISPT as a suitable sensor in the electrocatalysis and determination of 6-MP in an aqueous buffer solution. Continuously, the ability of this methodology for the determination of 6-MP in pharmaceutical and illness urines has been discussed. The detection limit, linear dynamic range, and sensitivity to 6-MP with MWCNTPE in the presence of

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mediator are comparable to, and even better than, those recently developed using voltammetric methods. Table 1 presents comparisons of the results obtained from the proposed method and those from electrochemical methods recently reported.

2. Experimental

2.1. Apparatus and reagents

All the voltammetric measurements were performed using an Autolab PGSTAT 302N, potentiostat/galvanostat (Utrecht, The Netherlands) connected to a three-electrode cell, Metrohm (Herisau, Switzerland) Model 663 VA stand, linked with a computer (Pentium IV, 1,200 MHz) and with Autolab software. A platinum wire was used as the auxiliary electrode. MWCNTPE and Ag/AgCl/KCl$_{sat}$ were used as the working and reference electrodes, respectively. The electrode prepared with carbon nanotubes was characterized by scanning electron microscopy (SEM) (Seron Tech. AIS 2100). A digital pH/mV-meter (Metrohm model 710) was applied for pH measurements. Spectrally pure graphite powder (particle size <50 μm) from Merck and multiwall carbon nanotubes (>90% MWCNTs basis, $d \times l = (110–70\ \text{nm}) \times (5–9\ \mu\text{m})$) from Fluka were used as the substrate for the preparation of the carbon paste electrode.

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. 6-MP and ISPT were from Fluka.

2.2. Preparation of the electrode

To eliminate metal oxide catalysts within the nanotubes, multiwalled carbon nanotubes were refluxed in the 2.0 M HNO_3 for 15 h, and then washed with twice-distilled water and dried at room temperature.

To obtain the best conditions in the preparation of the modified electrode, we optimized the ratio of MWCNTs in MWCNTPE. The results showed that the better CV shape and current was achieved with 10.0% (w/w) MWCNTs and 90.0% (w/w) graphite powder.

Graphite powder (0.900 g) was dissolved in diethyl ether, and hand mixed with 0.100 g carbon nanotubes in a mortar and pestle. The solvent was evaporated by stirring. A syringe was used to add paraffin to the mixture, which was mixed well for 40 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

2.3. Preparation of real samples

Five tablets of 6-MP (labeled 50 mg per table (Korea United Pharma, S. Korea)) were completely ground and homogenized. Then, 100 mg of the powders was accurately weighed and dissolved with ultrasonication in 100 ml of ethanol-water (1:1) solution (hot water). The resultant solution was diluted 100 times, and then 1.5 ml of the solution plus 10 ml of 40,000 μM buffer (pH 4.0) were used for the analysis. Drug-free human urine used in this study was obtained from healthy or non-healthy volunteers (from children with cancer-chronic lymphocytic leukemia). Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample were centrifuged for 5 min at 1500 rpm. The supernatant was diluted five times with universal buffer pH = 4.0. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method was used for the determination of 6-MP in real samples.

Table 1
Comparison of the efficiency of some electrochemical methods in the determination of 6-MP.

Electrode	Method	pH	Linear dynamic range (μM)	Limit of detection (μM)	Ref.
Glassy	Amperometry	7.0	0.4–100	0.2	[73]
Glassy	Amperometry	7.0	0.4–100	0.2	[74]
Carbon paste	Differential pulse voltammetry	9.0	0.09–350	0.06	[29]
Carbon paste	SWV	4.0	0.5–900	0.1	This work

2.4. Optimization of ISPT concentration

The influence of ISPT concentration on the peak currents was studied in the concentration range of 50–300 μM ISPT at pH 4.0. The results showed that by increasing the ISPT concentration up to 200 μM the net peak current increased, whereas further increasing the concentration of ISPT caused a decrease in the magnitude of the peak current. Therefore, 200 μM was selected as the optimal ISPT concentration.

2.5. Validation procedure

The linear dynamic range, limit of detection (LOD, based on S/N = 3), limit of quantification (LOQ, which measured as the lowest concentration of 6-MP in the linear calibration curve), repeatability, intermediate precision, recovery and selectivity were evaluated in the determination of 6-MP. The linear dynamic range was obtained by the linear sweep voltammetric analyzing of 6-MP solutions in the range of 0.1–900 μM. The LOD and LOQ were calculated from the linear calibration curve. Repeatability (intra-day) and intermediate (inter-day) precision were assessed at three concentrations. To assess the repeatability, three replicate measurements of each solution were made in a short period of time. To determine intermediate precision, the solutions were each analyzed three times per day for three consecutive days. The accuracy of procedure was verified by performing recovery assays in triplicate.

3. Results and discussion

3.1. Characteristics of the MWCNTPE

Fig. 1 shows SEM images for MWCNTPE and CPE. As it can be seen at a surface of CPE (Fig. 1A), the layer of irregular flakes of graphite powder presented was isolated from each other. After multiwall carbon nanotubes (MWCNTs) were added to carbon paste, it can be seen that MWCNTs were distributed on the surface of the electrode with special three-dimensional structure (Fig. 1B), indicating that the MWCNTs were successfully modified on the MWCNTPE.

3.2. Electrochemistry of the mediator

The cyclic voltammetric results showed a well defined and reproducible anodic and cathodic peak related to the ISPT$_{(Red)}$/ISPT$_{(Ox)}$ redox couple with quasi-reversible behavior, with peak separation potential of ΔE_p ($E_{pa} - E_{pc} = 230$ mV). These cyclic voltammograms were used to examine the variation of the peak currents vs. the potential scan rates. The plots of the anodic and cathodic peak currents were linearly dependent on $\upsilon^{1/2}$ at all scan rates. During the cyclic voltammetric experiments, the potential is linearly increased or decreased with $E(t) = E_{ini} \pm \nu t$, where $E(t)$ is the electrode potential as a function of t, ν is the potential scan rate and the signs "+" and "−" represent anodic scan and cathodic scan, respectively. Under the assumption that the redox couple is reversible, the surface concentrations of Ox and Red, i.e., $c_{Ox}(0,t)$ and $c_{Red}\,(0,t)$; respectively, are always

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